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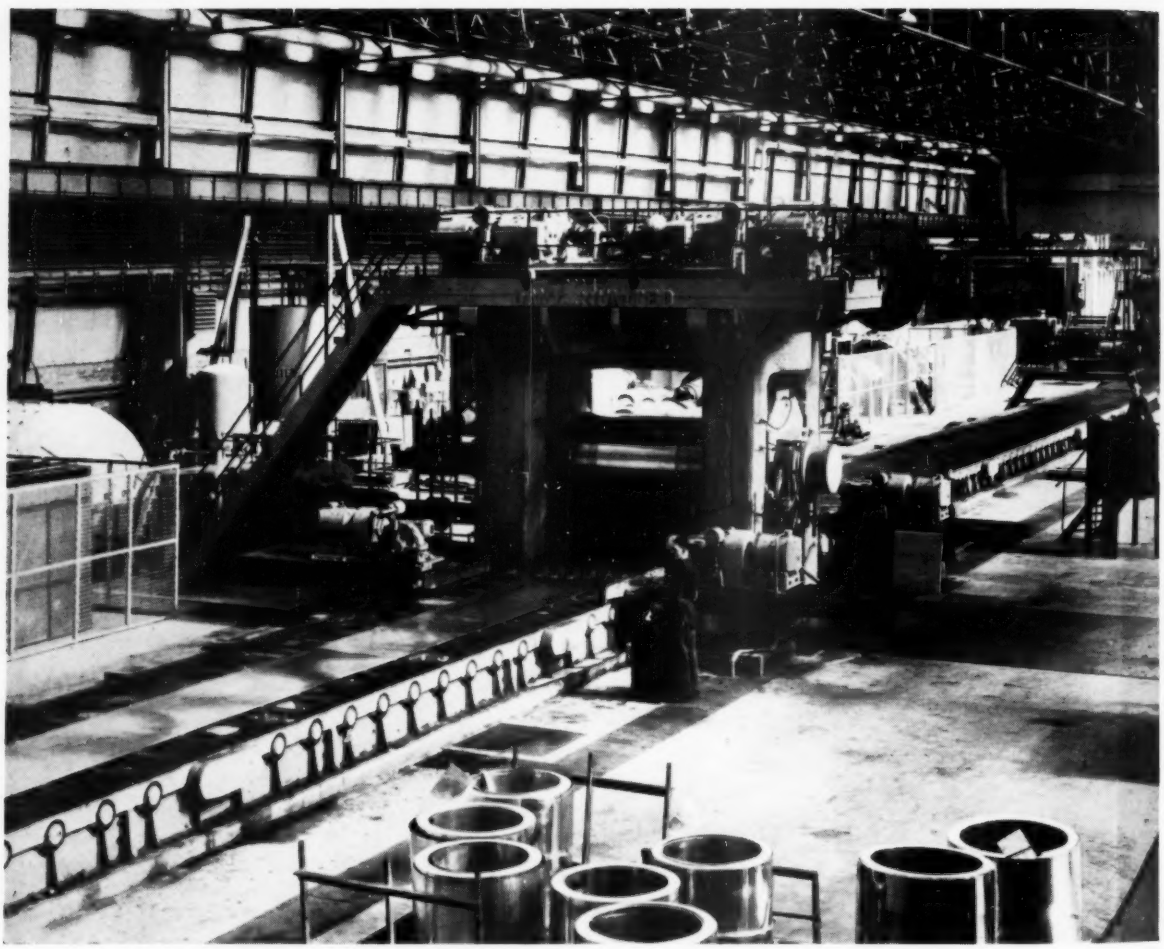

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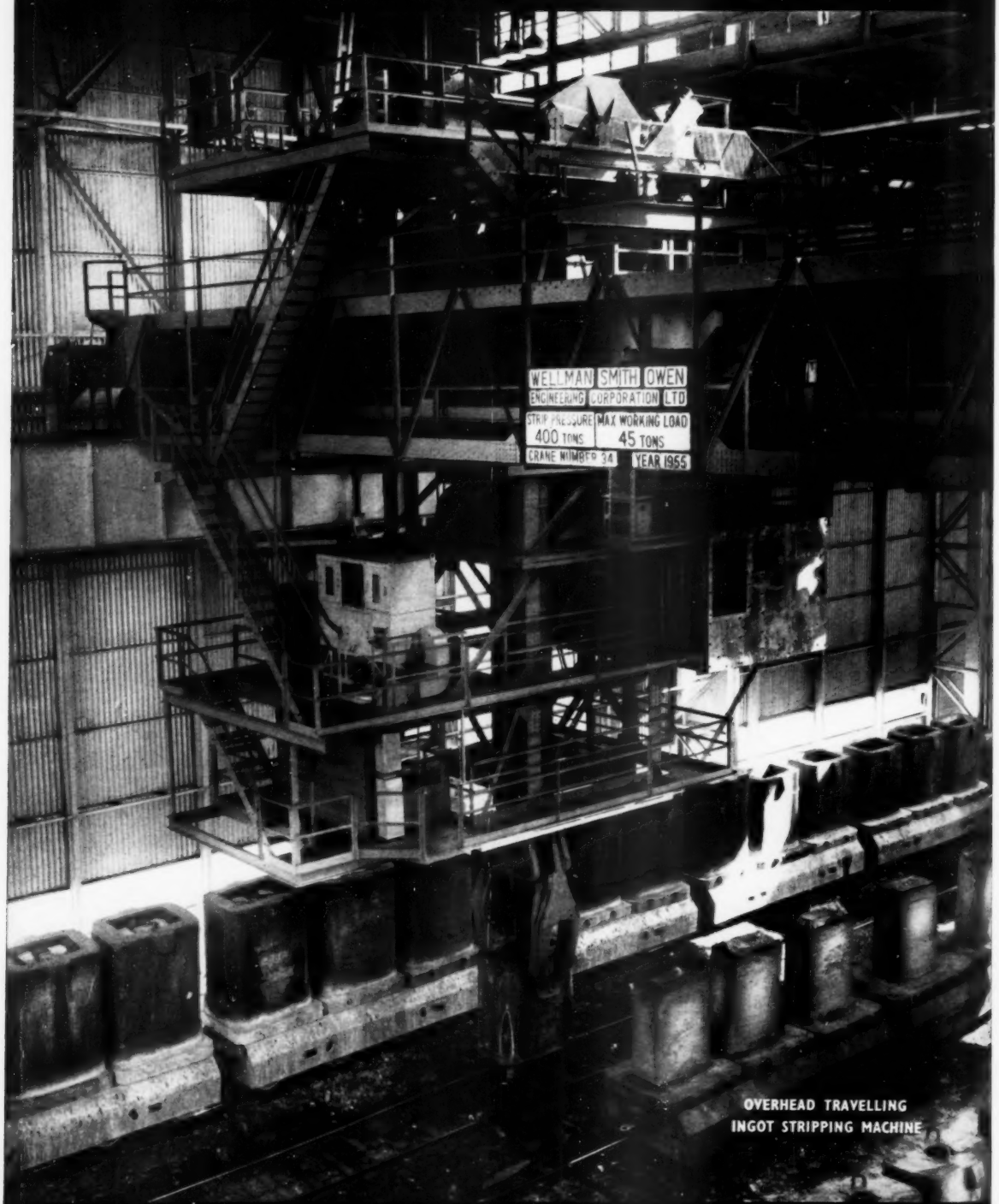

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Co-operation Wanted

ONE of the most used and abused words in the English language is "common sense"—for the trouble with common sense, in the way that it is often used, is that it is not so common. We are often inclined to regard as common sense something which seems perfectly obvious to us, although a Gallup Poll would undoubtedly show us to be in a minority. To the scientist it seems obvious that has had an important part to play in industry, but, although the position is improving, it is a view not universally appreciated in the business world. On the other hand, it must be admitted that the scientist may be inclined to minimise the important contribution to the national prosperity made by the business man. It was timely, therefore, that Sir Alexander Fleck, F.R.S., should devote a considerable part of his Presidential Address to this year's meeting of the British Association for the Advancement of Science to emphasizing the inter-dependence of science and business. These views should command wide respect, for not only is Sir Alexander a scientist of high standing, but, as Chairman of Imperial Chemical Industries, Ltd., he is one of the leading figures in the business world.

Scientific effort on the scale called for by the Second Industrial Revolution is estimated to cost this country £300 million, and if to this figure is added the cost of training the scientists necessary for its prosecution, the result is an extremely large sum, which, if the nation is to stay solvent, can only come from one source, the wealth we produce. The importance and responsibility of business, which produces and distributes most of national wealth, is obvious, since our capacity to extend our science and education largely depends on our ability to run business successfully.

Sir Alexander put forward three characteristics which a business should have if it is to survive and function effectively over a period of years. "First, it must contribute to the well-being of the community and its social evolution. I believe it can best do that in three specific ways: by producing goods or services for the community at fair prices; by giving fair treatment in the way of remuneration and working conditions to all who give their services to the business, whether as pay-roll employees, administrators or scientific staff; and by giving a fair return to those who risk their money in the business, so that, apart from this consideration, they will be encouraged to provide again for further ventures.

"Second, business must have the capacity to change its methods and, if necessary, even its objectives. It must be constantly alert to see that its products or services meet or anticipate the needs of the public, and to withstand the nipping and eager air of competition, whether it comes from advancing techniques or from new entrants into the field.

"Finally, if it is to be self-perpetuating through growth or modernisation, a business must dispose of its products or services for more than their cost—or, in plain language, it must make a profit. That is true of business whether run by private enterprise or by the State; nor does the political system of the State make any difference to the validity of this notion. Only from the excess of income over expenditure can we finance the expansion of business and science."

The growth of the output of manufacturing industry in the United Kingdom since the war has been at a greater rate than it was in the period between the wars. "If science has laid the foundation for much of this expansion," said Sir Alexander, "Business has provided the will and the means to complete the structure, and both must continue to do so." As we have stressed often in the past, our mineral resources are limited and declining, and the only way in which 50 million people can live at the standard enjoyed by the nation today, in an area too small to feed them, is by means of the goods produced by manufacturing industry and the services provided by finance and commerce—in other words, by business as a whole. Our standard of living—apart from complaints about it—tends to be taken for granted by some sections of the population who seem to think that the world owes us a living. A moment's reflection on the fact that 90% of the peoples of the world live in countries less prosperous than our own shows how wishful such thinking really is. We can only enjoy the living standards which our business enterprise and scientific knowledge enable us to earn through our exports.

Like all countries dependent on export trade, it is to our advantage to have economically and politically stable conditions throughout the world, but Sir Alexander believes that stability will not be achieved if plans for the industrialisation of the less developed territories are obstructed from a misconceived notion that we may thereby be able to retain our own markets for that much longer. "Our old staple exports of textiles, iron and steel, and coal, have long since given way to newer lines—vehicles, aircraft, machinery, chemicals and electrical goods. Even here the pattern keeps changing. Motor vehicles, fine and heavy chemicals and so on, are increasingly being manufactured in countries which previously produced only food or primary raw materials. We are therefore obliged to rely on selling things which no one else has yet learned to make, or make as cheaply, or on marketing skill and know-how."

There appears to be little doubt that at various times some of our traditional industries, in which we were pioneers, have suffered from the lack of proper scientific direction, which can only be achieved where the mutual inter-dependence of science and business is appreciated. That this is, unfortunately, not always so is illustrated by Sir Alexander's quotation from a managing director who wrote: "The place of the expert is not in the saddle but as the assistant and the adviser. The scientist must be on tap, not on top."

Commonwealth Uranium Search

THE part played by the Atomic Energy Division of the Geological Survey in the search for uranium is little known because of the security measures that have applied until comparatively recently to information on the production of nuclear raw materials. The Division, which is the youngest branch of the oldest organization now in the Department of Scientific and Industrial Research—the Geological Survey of Great Britain—was created during the Second World War to investigate the exploitation and supply of uranium and other strategic materials. Since that time, it has played an important part in bringing uranium properties into production, and in organizing and stimulating the search for the raw materials of atomic energy in many of the countries of the Commonwealth. Close co-operation is maintained between the Division and the Atomic Energy Authority, on whose behalf the work is undertaken.

The Atomic Energy Division has grown to be a major branch of the Geological Survey, and the assistance it can give ranges from radiometric assaying and the preparation of mineralogical reports to field surveys and the assessment of new discoveries of mineralisation made by prospectors and mining companies. For example, in 1957, field investigations were carried out in the Union of South Africa, British Guiana, Jamaica, Sierra Leone, Bechuanaland, Ghana, Nigeria, Nyasaland, Southern Rhodesia and New Zealand, in addition to field work in Britain.

Last year the Atomic Energy Division of the Geological Survey, acting on behalf of the Atomic Energy Authority, undertook an airborne radiometric survey of West and Central Cornwall. Results of this survey have so far been interesting. Several of the anomalies recorded are sufficiently marked at surface to merit pitting, trenching and exploratory drilling to prove the extent of the mineralization underground. The area to be covered by airborne survey will be extended this year to cover the remainder of Cornwall, and much of Devon and Somerset. Any areas which seem to justify closer examination will be investigated by ground parties equipped with portable scintillation and Geiger-Muller counters.

In addition to this air reconnaissance survey, the Division is undertaking the examination of abandoned mine workings in Cornwall where small amounts of uranium are known to occur. Only surface, or near surface, examination has hitherto been possible, but reconnaissance drilling started a few months ago has continued on an increased scale during the summer. The Division may later expand its survey to cover other areas in which uranium mineralization might occur ; for example, North and Central Wales, North England and the Southern Uplands of Scotland.

Field work of this type is of little value without research facilities behind it. Behind the scenes, in the Division's laboratories, the potential ores are examined in detail—a less spectacular yet vitally important task. Radioactive mineral specimens found in the field—either by the Geological Survey's own geologists, by other geological surveys, by mining companies or by private prospectors—are studied by the most modern techniques, some of which have been developed by members of the Division.

An indication of the complexity of the work undertaken may be obtained from the fact that there are over a hundred known uranium-bearing minerals and over fifty thorium-bearing minerals. Thousands of samples are normally examined annually and, at the same time, a research programme is maintained which has enabled the Division to make a considerable contribution to radiogeology in papers published, from time to time, in *The Bulletin of the Geological Survey* and other scientific journals. Studies of world-wide importance have been made in the fields of mineralogy and ore genesis, autoradiograph techniques, ore mineral identification, and the examination of radioactive minerals by X-ray methods.

To mining companies, private prospectors, including members of the public, the Division provides on behalf of the Atomic Energy Authority a free assay service for material which is considered to be radioactive. The only proviso in accepting material is that full details of locality must be given. This information is, of course, treated as confidential.

An idea of the effort involved in the detailed examination of rock samples can best be seen by tracing one through the laboratories. When specimens are received they are examined first by a specially constructed Geiger-counter, which gives a rough indication of whether or not the material is abnormally radioactive. If the latter, representative portions of the specimens are crushed for accurate assay by radiometric techniques, and the content of uranium or thorium estimated. Sections from the specimens are then cut by diamond saw and mounted for examination under the microscope. The sections of relatively transparent minerals are mounted on glass slides and rubbed down till they are about a thousandth of an inch thick ; those of the more opaque species are examined by reflected light after polishing. Usually the minerals comprising the specimen can be identified in this way, but it may be necessary to remove minute fragments of any undetermined mineral for examination by X-ray diffraction. The photographs obtained by this latter technique are characteristic of the particular mineral species. When radioactive minerals are exposed on special emulsions, similar to those used on photograph plates, they produce an image or autoradiograph on development. Use is made of this phenomenon in the location of radioactive mineral grains and in their identification. Associated non-radioactive minerals in the specimens must also be identified, as the nature of these to a large extent dictates the technique that may have to be employed later in extracting the uranium or thorium.

The end-product of such an investigation is a report on each specimen or group of specimens submitted. This gives details of the uranium or thorium content and the nature of the minerals contributing to the radioactivity, with their grain size and distribution in relation to the associated non-radioactive minerals. Attention is also paid in such reports to specific problems, such as the bearing of the mineralogical observations on difficulties that may be encountered in treating material of ore grade.

Dollar Order for Furnaces

WILD-BARFIELD ELECTRIC FURNACES, LTD., have recently received from the United States an order for twenty-eight 750 lb. capacity mains frequency induction heated aluminium holding furnaces, valued at nearly $300,000. This order was received in the face of severe competition from American furnace manufacturers.

Pure Torsion Creep Tests on Magnesium Alloy (2% Al) at 20° C., and on 0·2% C Steel at 450° C., at Low Rates of Strain (10^{-6} to 10^{-9} per hour)

By A. E. Johnson, D.Sc., M.Sc.Tech., M.I.Mech.E., J. Henderson, B.Sc., Grad. Inst. P., and V. D. Mathur, B.Sc.

Mechanical Engineering Research Laboratory, East Kilbride.

In this paper are presented and discussed the results of pure torsion creep tests at stresses giving rise to creep rates of order 10^{-3} per hour to 10^{-9} per hour in a cast magnesium alloy and a cast carbon steel. Creep strain for each of the materials shows a dependence on time which does not alter throughout the range of creep rates concerned. The stress dependence, in addition to terms of more than unit power, noted at normally investigated levels of creep rate, also includes a term of unit power stress dependence, representing a recoverable element of creep, which becomes increasingly dominant at the lower rates.

VIRTUALLY all investigations of the creep of metals at elevated temperatures have concerned themselves with the measurement of rates of not lower order than about 10^{-7} per hour. This has been so for two reasons. Firstly, many of the requirements of industrial designers have been adequately satisfied by data concerning rates of this order, and, secondly, no equipment capable of measuring rates of a lower order at elevated temperatures has been available.

Whilst the first reason is still largely valid, it is not completely so, since certain users of high-temperature materials have expressed an interest in the creep properties of such materials at relatively low stress levels, in order to satisfy certain new industrial demands of the Atomic Energy Authority. The second reason was removed by the design by one of the authors some few years ago of a torsion creep unit capable of giving measurement of creep rates of order down to 10^{-9} per hour. This machine was fully described in Reference 1, and is not further referred to in this paper.

Apart from any industrial interest in low levels of creep rate, there is, of course, an academic interest since, generally speaking, information gained at these levels may well yield evidence concerning the mechanism of creep. The creep characteristics of metals at normal levels of creep rate as expressed by the log-stress/log-creep-rate curve are normally shown to be a curve of two main branches of different slope, the branch at lower stress levels having the steeper slope. The values of these slopes correspond to power terms in complex expressions relating the creep strain or rate to stress. In the authors' opinion it appeared that at the lowest levels of creep rate, since an increasingly large proportion of the creep strain would be likely to be of a recoverable nature, the log-stress/log-creep-rate characteristic curve would be likely to display a further inflexion, this branch of the curve tending to represent increasing unit stress dependence of the creep, since such dependence is characteristic of recoverable or anelastic strain, that is to say that the characteristic log-creep-rate/log-stress curve would terminate with a slope of 45°. Confirmation of this matter was sought in the work carried out.

TABLE I.—DETAILS OF PRODUCTION, HEAT TREATMENT AND CHEMICAL COMPOSITION OF MATERIALS

Material	Details of Production and Dimensions	Details of Heat Treatment	Details of Chemical Composition (%)									
			Zn	Al	Si	Cu	Mn	Fe	Sn	Mg		
Magnesium Alloy	Billet—diameter 12 in.; length 12 in.	Soaked for 4 hours at 480 ± 5° C., and furnace cooled to room temperature in about 10 hours. Heat treatment carried out in atmosphere of sulphur dioxide.	<0·05	2·0	0·02	<0·01	0·03	<0·04	<0·03	Remainder		
			C	Si	S	P	Ni	Cr	Mo	Cu	Sn	Mn
Carbon Steel	Core from an ingot—diameter, 16 in.; length, 34½ in.	Soaked for 4 hours at 840–850° C., and air cooled as uniformly as possible. Reheated to 500–600° C. and soaked for 4 hours. Cooled in furnace.	0·24	0·22	0·036	0·033	0·27	0·09	0·03	0·16	0·005	0·69

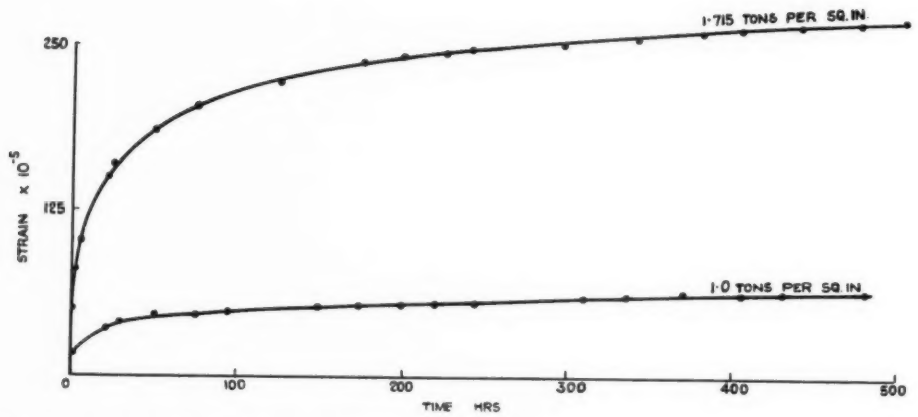

Fig. 1.—Pure torsion creep tests on magnesium alloy (2% Al) at 20° C. Creep-strain/time curves. Curves shown are to composite curve form.

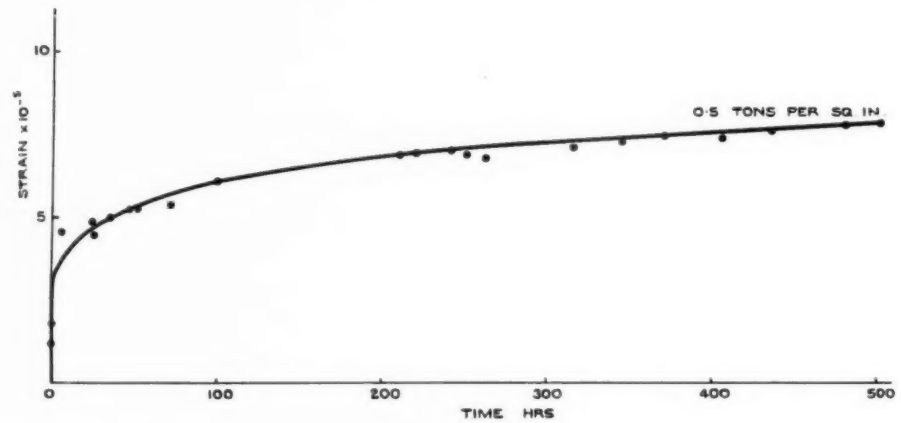

Fig. 2.—Pure torsion creep tests on magnesium alloy (2% Al) at 20° C. Creep-strain/time curve. Curve shown is to composite curve form.

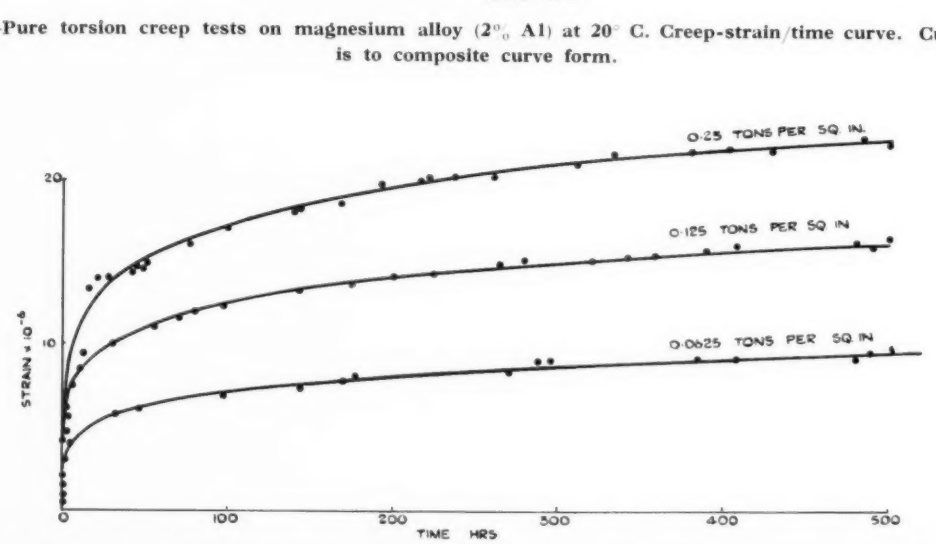

Fig. 3.—Pure torsion creep tests on magnesium alloy(2% Al) at 20° C. Creep-strain/time curves. Curves shown are to composite curve form.

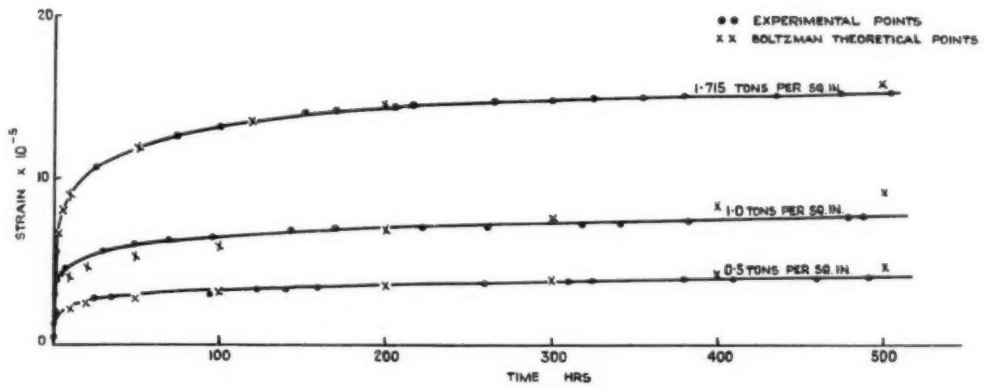

Fig. 4.—Pure torsion creep tests on magnesium alloy (2% Al) at 20° C. Creep-recovery/time curves. Curves shown are to composite curve form.

Details of Materials

The materials concerned were, firstly, a continuously cast magnesium alloy containing 2% aluminium and, secondly, a cast 0·2% carbon steel. Details of composition and preparation of these two materials are given in Table I. Both materials had been shown in previous work to be very isotropic as regards their creep properties in all directions of the original billet. Further details concerning the preparation, microstructure, and isotropy of the magnesium alloy may be found in Reference 2.

Experimental Procedure

The tests were carried out in the M.E.R.L. high-sensitivity torsion creep unit,[1] the specimens being of 8-in. parallel length, of 1 in. internal diameter., and of $1\frac{1}{8}$ in. external diameter. In view of the increased significance of relative specimen condition in tests at these low rates of strain, very great care in heat treatment and machining was taken to render the condition of all specimens as similar as possible. The furnace used for the tests was thermostatically temperature controlled to $\pm \frac{1}{4}$° C., and a temperature gradient along the test piece of not more than 3–5° C. was aimed at.

Six creep tests of 500 hours' duration, followed by 500 hours of recovery under zero load, were made on the magnesium alloy at 20° C. under stresses of $1·71_5$, 1·0, 0·5, 0·25, $0·12_5$ and $0·06_{25}$ tons/sq. in. Likewise, six similar creep and recovery tests were made on the carbon steel at 450° C. under stresses of 3, 2, 1·5, 1·0, 0·5 and 0·25 tons/sq. in. Readings of creep strain were made at least twice per day in all cases.

Experimental Results

The results of the creep tests on the magnesium alloy are given in Figs. 1–3 which show the creep-strain/time curves, while the results of the corresponding recovery tests are shown in Figs. 4 and 5. In the case of the creep tests on carbon steel, the creep-strain/time curves are shown in Figs. 8, 9 and 10, while the corresponding recovery curves are shown in Figs. 11, 12 and 13.

Figs. 6 and 14, for the magnesium alloy and the carbon steel, show respectively the log-creep-strain/log-time curves of the forward creep tests, while Fig. 7 and Figs. 15 and 16 show for the two materials certain relations derived from the experimental results.

Discussion of Results

(a) Creep Tests on Magnesium Alloy at 20° C.

The six stresses used in this section of the work are listed in Table II, where are also given the creep rates

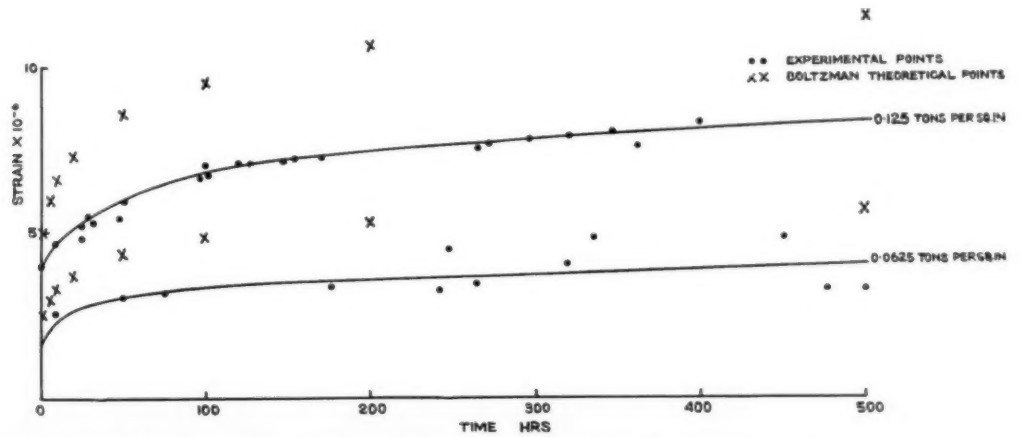

Fig. 5.—Pure torsion creep tests on magnesium alloy (2% Al) at 20° C. Creep-recovery/time curves. Curves shown are to composite curve form.

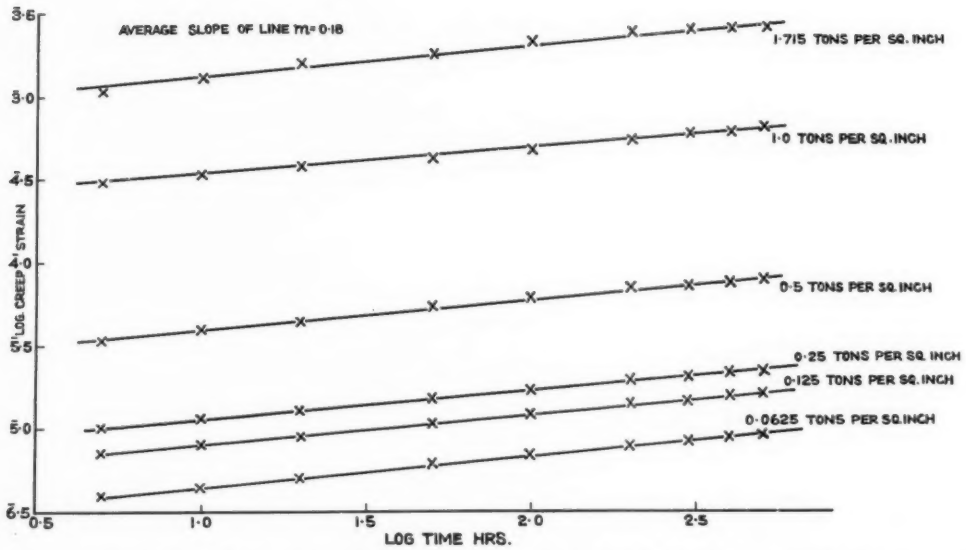

Fig. 6.—Pure torsion creep tests on magnesium alloy (2% Al) at 20° C. Log-creep-strain/log-time curves.

measured at 500 hours. It will be noted that these rates range from 600×10^{-9} to 2×10^{-9}. Referring to the forward creep curves of Figs. 1–3, it will be noted that they have a common curve form.

In Fig. 6 for these tests, log creep strain is plotted against log time, and as will be seen, a series of parallel lines of slope corresponding to a power dependence of creep strain upon time of 0·18 represents closely the mean trend of the experimentally derived data. The creep-strain/time relation is thus of the nature :—

$$\text{creep strain} = At^{0\cdot18}$$

where A may be a complex function of stress. The values of A corresponding to the individual lines of Fig. 6 were computed and are plotted in Fig. 7. Analysis showed that a good mean line to the experimental points in this figure corresponded to a relation :—

$$A = [3\cdot5 \times 10^{-5}S + 1\cdot5 \times 10^{-4}S^{2\cdot86}]$$

which in turn corresponded to a relation :—

$$\text{creep strain} = [3\cdot5 \times 10^{-5}S + 1\cdot5 \times 10^{-4}S^{2\cdot86}]t^{0\cdot18}.$$

At lower stresses a sufficient approximation was given by the term $A = 3\cdot5 \times 10^{-5}S$ alone.

Considering the physical significance of this equation, it was noted that the power exponent (2·86) for the second stress term corresponded with what had been indicated by previous complex stress creep investigations on this material at 20° C., in which creep strains corresponding to rates of order 10^{-6} and upwards had shown a power stress dependence of between 2 and 3. Secondly, the first term of unit stress dependence was taken possibly to correspond with recoverable creep, and this point was borne in mind in analyzing the creep recovery tests on this material.

Accordingly it is evident that, in this region of low creep rates, the log-stress/log-creep-strain or creep-rate characteristic curve will show a region of changing slope running eventually into a 45° slope corresponding to largely anelastic or recoverable creep. This change will not be noticeable by measurement with creep equipment of normal accuracy.

(b) Creep Recovery Tests on Magnesium Alloy at 20° C.

As indicated in the previous section, it appears likely that a proportion of creep occurring in the forward creep tests was of a recoverable nature, and that this was represented by the term in the creep strain relation $3\cdot5 \times 10^{-5}S\,t^{0\cdot18}$. Accordingly, in analyzing the recovery curves shown in Figs. 4 and 5, it was decided as a first step to examine the applicability of a simple Boltzmann superposition relation to the results.

The Boltzmann superposition or memory theory, of course, postulates that strain due to both the loading and unloading actions of the composite creep/creep-recovery test continues to the end of this test. Thus (as in the experiments), if a creep test of 500 hours be succeeded by an equally long recovery test, then the *total* strain at time t in the recovery test is $A[(500 + t)^{0\cdot18} - t^{0\cdot18}]$ if the strain be proportional to $t^{0\cdot18}$. A for the present material has, of course, the value $[3\cdot5 \times 10^{-5}]S$. The actual measured recovery strain, however, is the total strain less the forward creep strain at the end of the creep test alone, i.e. in the case of the present tests, $500^{0\cdot18}$, i.e. recovery strain in the present case

$$= \{[3\cdot5 \times 10^{-5}S][(500 + t)^{0\cdot18} - t^{0\cdot18} - 500^{0\cdot18}]\}.$$

The values of this theoretical strain were computed for the various stresses involved in the currently considered tests, and are shown plotted in Figs. 4 and 5 alongside the experimental recovery curves.

Considering the individual tests, it is seen that at 1·715, 1·0 and 0·5 tons/sq. in., the measure of agreement between Boltzmann theory and experimental results is close. The recovery test at 0·25 ton/sq. in. was unfor-

TABLE II.—TORSIONAL CREEP RATES AT 500 HOURS FOR MAGNESIUM ALLOY AT 20° C.

Stress (tons/sq. in.)	Torsional Creep Rate at 500 Hours (in./in./hr.)
$1\cdot71_5$	560×10^{-9}
1·0	130×10^{-9}
0·5	16×10^{-9}
0·25	$4\cdot8 \times 10^{-9}$
0·125	$3\cdot4 \times 10^{-9}$
0·0625	$1\cdot8 \times 10^{-9}$

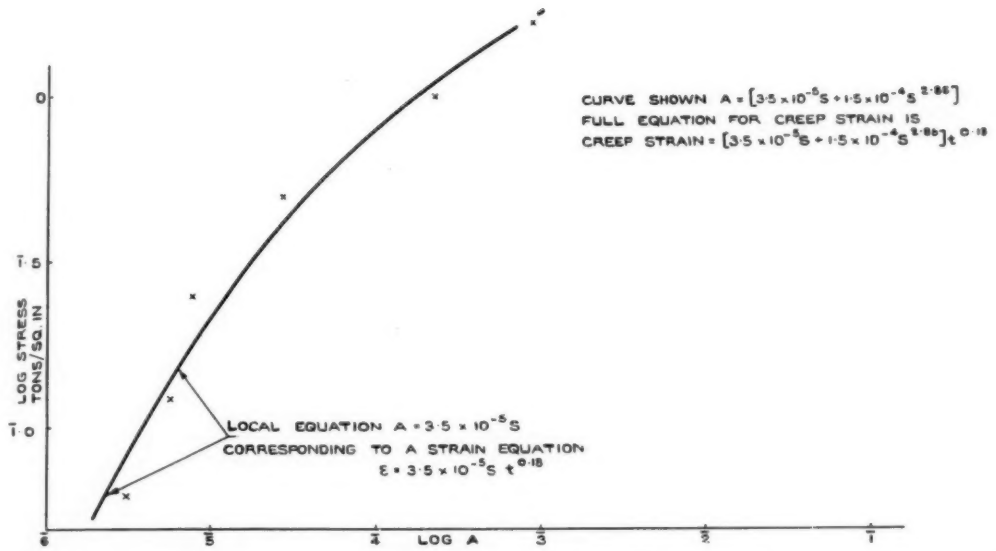

Fig. 7.—Pure torsion creep tests on magnesium alloy (2% Al) at 20° C. Relation: log-stress/log-A in equation: forward creep strain = $At^{0.18}$

tunately spoiled by accidental overheating. In the case of the two remaining tests, the Boltzmann relation gave high results, but having regard to the considerable effect of the condition of individual specimens at these low orders of strain, it is doubtful whether the disagreement shown by the experimental data and the predictions of Boltzmann theory is outside the bounds of scatter, due to material conditions, or imposed experimental procedure. If the above point be accepted, it appears reasonable to say that for this material and temperature, the total creep strain includes an anelastic element which quite closely follows the Boltzmann superposition principle in its most simple form.

(c) *Creep Tests on Carbon Steel at 450° C.*

The six stresses used in this section of the work are listed in Table III, where are also given the creep rates measured at 500 hours. These rates range from 100×10^{-9} to 5×10^{-9} per hour. As in the case of the magnesium alloy it will be noted that the creep curves have a common curve form.

The log-creep-strain/log-time plot of these curves (see Fig. 14) shows a series of parallel lines, well representing the experimental points and corresponding in slope to a power dependence of creep strain upon time of 0·26. The creep-strain/time relation is thus of the nature :—

$$\text{creep strain} = At^{0.26}$$

where A may be a complex function of stress. Following the procedure adopted in the case of the magnesium alloy, the values of A corresponding to the individual lines of Fig. 14 were computed and plotted in Fig. 15.

TABLE III.—TORSIONAL CREEP RATES AT 500 HOURS FOR 0·2% CARBON STEEL AT 450° C.

Stress (tons/sq. in.)	Torsional Creep Rate at 500 Hours (in./in./hr.)
3	100×10^{-9}
2	40×10^{-9}
1·5	33×10^{-9}
1	28×10^{-9}
0·5	10×10^{-9}
0·25	5×10^{-9}

In this case it appears obvious that a linear slope of 45°, presumably corresponding to anelastic creep, well represents the experimental data in this diagram at the lower stress levels. However, a departure from this linear relation is obvious at the higher stress levels, but unfortunately the trend of the available points is obviously not sufficiently well established to enable the mean curve equation to be determined with any real certainty.

However, it was a fortunate circumstance that a number of pure torsion creep tests on specimens of 0·5-in. internal diameter and 0·02-in. wall thickness had been made in connection with the complex stress creep research, and this family of tests (in conjunction, of course, with corresponding complex stress creep tests) had provided data which had been subject to very thorough analysis in regard to the dependence of creep rate at 150 hours upon stress and time.

While recognizing that differing specimen size would be likely to introduce a scale factor which would make itself felt in the creep-rate/stress analysis, it was hoped that the information available from this source would throw some light upon the present problem. Accordingly, for the current series of tests, creep rates were measured at 150 hours and are plotted log-log against stress in Fig. 16. Also plotted in this figure are a series of points corresponding to the pure torsion creep tests of the complex stress series referred to previously. The line drawn through these later points corresponds to an equation derived in the analysis of the complex stress tests which, in terms of torsion stress and rate, becomes :

$$C_c = [AS^{3.45} + BS^{7.7}]t^{-0.7},$$

A and B being values appropriate to the specimen size.

In the previous series of tests the creep strain was proportional to $t^{0.26}$. The creep rate is accordingly proportional to $t^{-0.74}$. While this differs from the exponent indicated above, it is sufficiently close to suggest that the two stress exponents indicated in the relation may well be representative of the current tests.

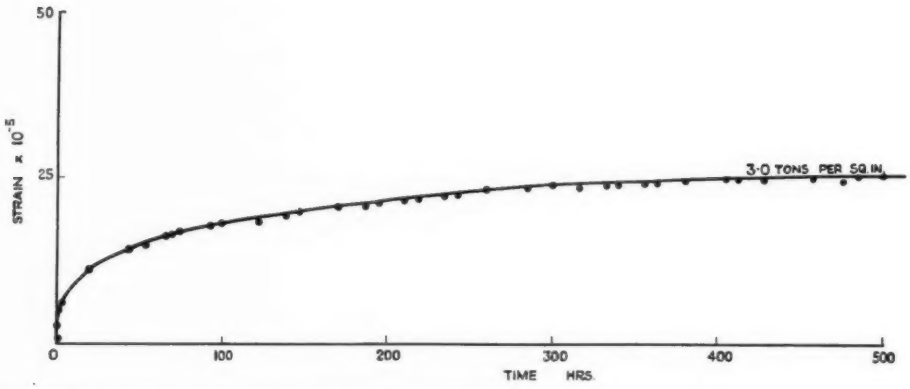

Fig. 8.—Pure torsion creep tests on 0·2% carbon steel at 450° C. Creep-strain/time curve. Curve shown is to composite curve form.

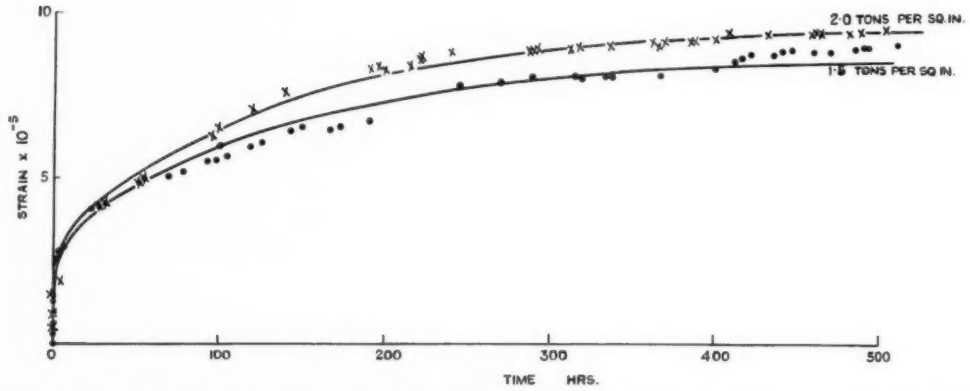

Fig. 9.—Pure torsion creep tests on 0·2% carbon steel at 450° C. Creep-strain/time curves. Curves shown are to composite curve form.

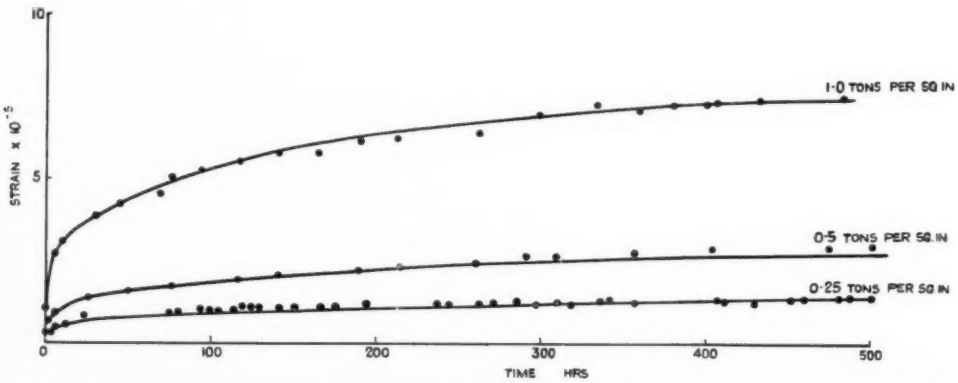

Fig. 10.—Pure torsion creep tests on 0·2% carbon steel at 450° C. Creep-strain/time curves. Curves shown are to composite curve form.

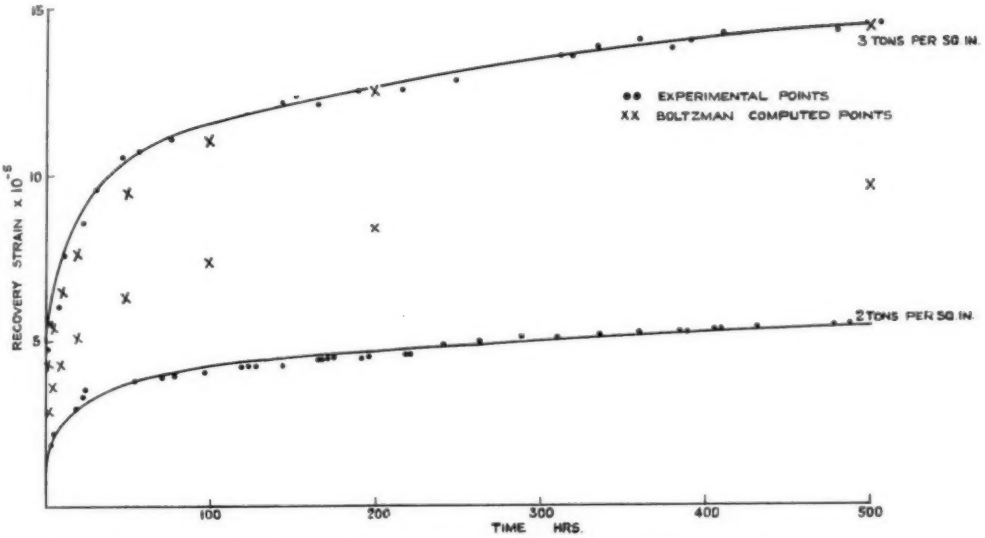

Fig. 11.—Pure torsion creep tests on 0·2% carbon steel at 450° C. Creep-recovery/time curves. Curves shown are to composite curve form.

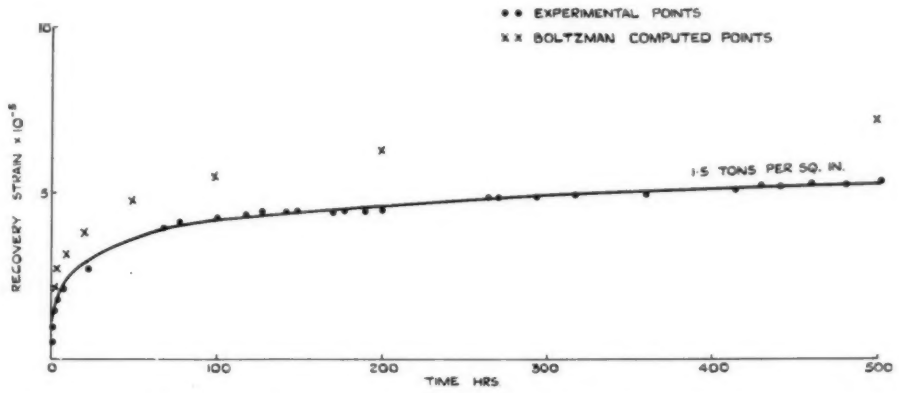

Fig. 12.—Pure torsion creep tests on 0·2% carbon steel at 450° C. Creep-recovery/time curve. Curve shown is to composite curve form.

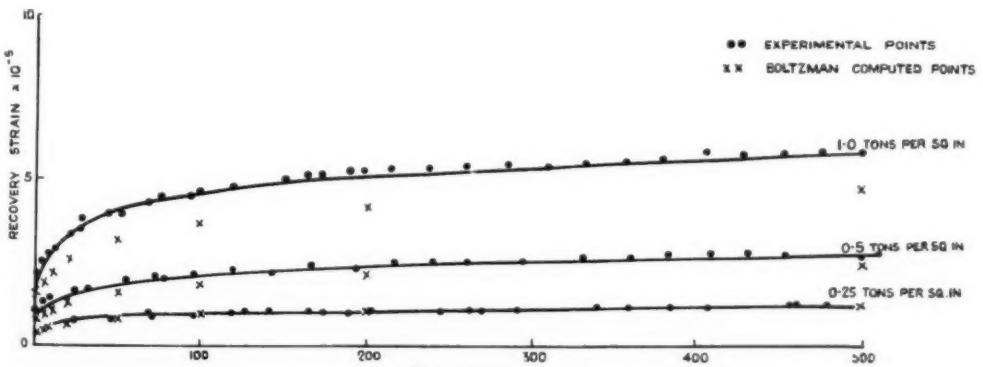

Fig. 13.—Pure torsion creep tests on 0·2% carbon steel at 450° C. Creep-recovery/time curves. Curves shown are to composite curve form.

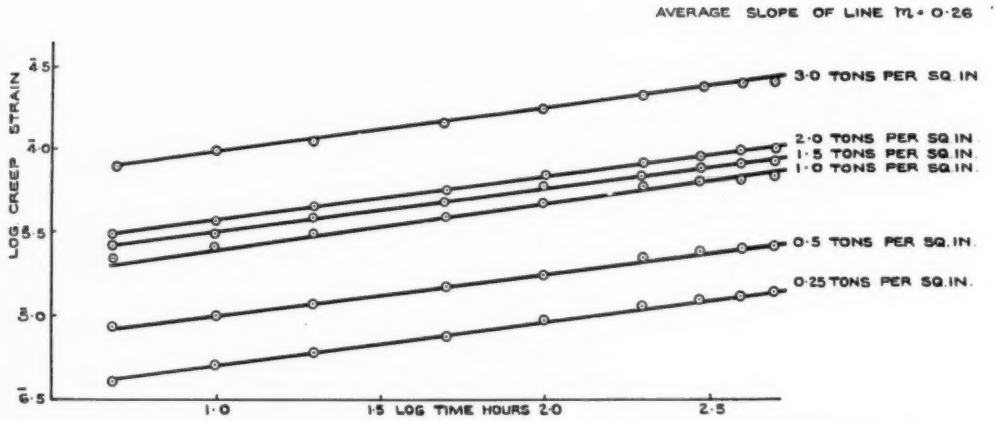

Fig. 14.—Pure torsion creep tests on 0·2% carbon steel at 450° C. Log-creep-strain/log-time curves.

It also seemed likely that, since the difference between the current specimens and those of the complex stress tests was probably not large, the ratio of the values of constants A/B would remain the same, and that the actual values would not greatly differ from those obtained in the complex stress creep tests. With these postulates in mind, a mean curve was drawn through the lower level stress points of the current series of tests, and was found to correspond to a locally approximate relation :—

$$C_c = [3{\cdot}1 \times 10^{-6}S]\, t^{0{\cdot}74}.$$

By trial, a series of terms $AS^{3{\cdot}45} + BS^{7{\cdot}7}$ (where A and B did not greatly differ from the values of the complex stress tests, and retained the same ratio) were in turn added to the term $[3{\cdot}1 \times 10^{-6}S]$, and the fit of the resulting total curves was examined. The best of these is shown in Fig. 16 and actually corresponded to the relation :—

$$C_c = [3{\cdot}1 \times 10^{-6}S + 2 \times 10^{-7}S^{3{\cdot}45} + 3 \times 10^{-11}S^{7{\cdot}7}]\, t^{0{\cdot}74}$$

It will be seen that the curve corresponding to this relation is first of all a good mean of the experimental points, and secondly runs close to the curve shown for the torsion tests of the complex stress research, showing a remove from the latter which seems quite likely to correspond to the effect of differing specimen size. Accordingly, it appears reasonable to regard this curve as well representing the behaviour in the current tests.

Having accepted this point, the curve of log A/log-stress corresponding to this relation was plotted in Fig. 15, the highest power stress term being ignored, since at such stress levels this term had a trivial value. The relation became :—

$$A = [1{\cdot}19 \times 10^{-5}S + 7{\cdot}67 \times 10^{-7}S^{3{\cdot}45}],$$

corresponding to a strain relation :—

$$\text{creep strain} = [1{\cdot}19 \times 10^{-5}S + 7{\cdot}67 \times 10^{-7}S^{3{\cdot}45}]\, t^{0{\cdot}26}.$$

In this relation it was tentatively regarded as likely that the term $[1{\cdot}19 \times 10^{-5}St^{0{\cdot}26}]$ represented recoverable creep and this point was borne in mind in analyzing the recovery tests for this material.

(d) Creep Recovery Tests on Carbon Steel at 450° C.

It was indicated in the previous section that a propor-

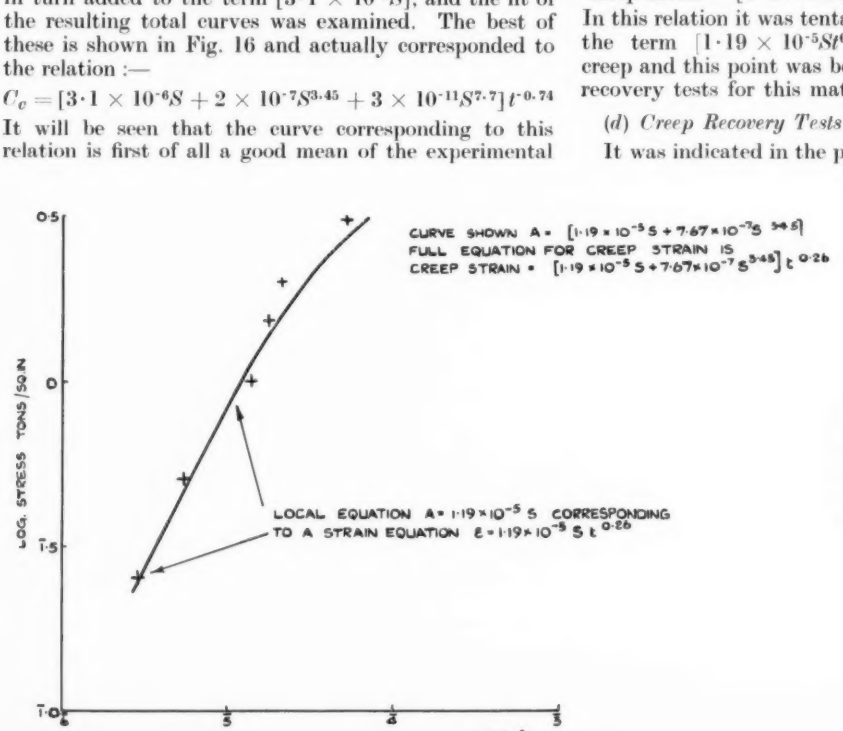
CURVE SHOWN A = [1·19 × 10⁻⁵ S + 7·67 × 10⁻⁷ S 3·45]
FULL EQUATION FOR CREEP STRAIN IS
CREEP STRAIN = [1·19 × 10⁻⁵ S + 7·67 × 10⁻⁷ S 3·45] t 0·26
LOG. STRESS TONS/SQ.IN
0·5
0
1·5
1·0
LOCAL EQUATION A = 1·19 × 10⁻⁵ S CORRESPONDING
TO A STRAIN EQUATION ε = 1·19 × 10⁻⁵ S t 0·26
LOG. A

Fig. 15.—Pure torsion creep tests on 0·2% carbon steel at 450° C. Relation: log-stress/log-A in equation : forward creep strain = $At^{0{\cdot}26}$

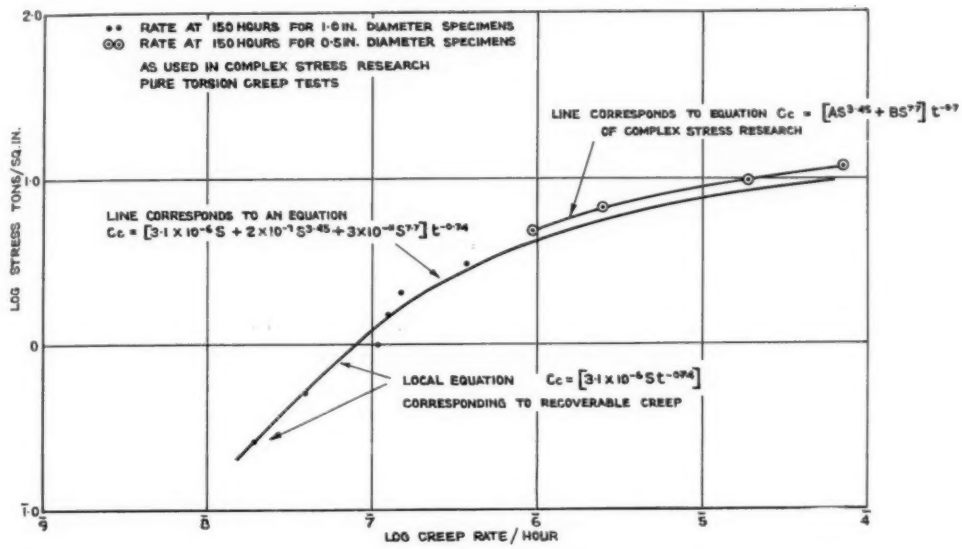
•• RATE AT 150 HOURS FOR 1·0 IN. DIAMETER SPECIMENS
⊙⊙ RATE AT 150 HOURS FOR 0·5 IN. DIAMETER SPECIMENS
AS USED IN COMPLEX STRESS RESEARCH
PURE TORSION CREEP TESTS
LINE CORRESPONDS TO EQUATION Cc = [AS^3·45 + BS^7·7] t^-0·7
OF COMPLEX STRESS RESEARCH
LINE CORRESPONDS TO AN EQUATION
Cc = [3·1 x 10^-6 S + 2 x 10^-31 S^3·45 + 3 x 10^-48 S^7·7] t^-0·74
LOCAL EQUATION Cc = [3·1 x 10^-6 S t^-0·74]
CORRESPONDING TO RECOVERABLE CREEP
LOG STRESS TONS/SQ.IN.
LOG CREEP RATE / HOUR

Fig. 16.—Pure torsion creep tests on 0·2% carbon steel at 450° C. Relation: log-stress/log-creep-rate-per-hour at 150 hours.

tion of creep in the forward creep tests was of a recoverable nature, and that this was represented by the term in the creep strain relation $[1{\cdot}19 \times 10^{-5}S]\ t^{0.26}$. As in the case of the magnesium alloy at 20° C., it was decided to commence analysis by examining the applicability of a Boltzmann superposition relation to the data. In this case (again following the argument of Section (*b*)), the recovery strain was given upon the Boltzmann theory by the relation :—

recovery strain =

$$[1{\cdot}19 \times 10^{-5}S]\ [(500 + t)^{0.26} - t^{0.26} - 500^{0.26}].$$

The values of this theoretical strain were computed for the various stresses and are shown plotted in Figs. 11, 12, and 13 against the experimental recovery data. At 3 tons/sq. in. agreement between this data and Boltzmann theory is good. At 2 tons/sq. in. Boltzmann theory gives high results—roughly twice the value of the experimental strain. At 1·5 tons/sq. in. Boltzmann theory gives somewhat high results, and at 1·0 ton/sq. in. the results are low, but not greatly so, whilst at 0·3 and 0·25 ton/sq. in. agreement is close.

Accordingly, with the exception of the test at 2 tons/sq. in., the picture is much as for the magnesium alloy, and suggests that for the 0·2% carbon steel at 450° C., with due regard to the effect of individual specimen condition, it must be conceded that Boltzmann theory represents the recoverable strain quite well.

Conclusion

The continuously cast magnesium alloy at 20° C. and the cast carbon steel at 450° C. have displayed similar physical features in the range of creep rates 10^{-7} to 10^{-9}. The materials in themselves are sufficiently intrinsically different in nature to suggest that these physical features may be indicative of the creep behaviour of an appreciable number of metals at low rates of creep strain.

Within the range of stress levels giving rise to creep rates of order 10^{-6} per hour to 10^{-9} per hour, creep strain for each of the materials shows a dependence on time which does not alter throughout the range of creep rates concerned. The stress dependence, in addition to more than unit power terms noted at normally investigated levels of creep rate, also included a term of unit stress dependence, which became increasingly dominant at the lower rates. This term represented a recoverable element of creep which for both materials appeared to be reasonably well represented by a Boltzmann superposition principle in its most simple form.

Acknowledgments

The work described is part of the research programme of the Mechanical Engineering Research Board of the Department of Scientific and Industrial Research, and is published by permission of the Director of the Mechanical Engineering Research Laboratory.

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1 Johnson, A. E. A High-Sensitivity Torsion Creep Unit, *Journal Scientific Instruments*, **27**, (3), March 1950, 74.
2 Johnson, A. E. The Creep of a Nominally Isotropic Magnesium Alloy at Normal and Elevated Temperatures under Complex Stress Systems. *Metallurgia*, **42**, (252), October 1950, 249.

Correction

New Magnesium Alloys

We regret that an error appeared in the caption to Fig. 1, on page 68 of the August issue of Metallurgia, in that the casting was described as having a maximum section thickness of $1\frac{1}{8}$ in., whereas in fact this figure was the minimum section thickness.

Change of Address

The new address of the London Office of Steele and Cowlishaw, Ltd., is Westwood House, Swallow Street, Piccadilly, London, W.1 (Tel. Regent 8301): the office at High Holborn is now closed.

New Beryllium Plant

IMPERIAL CHEMICAL INDUSTRIES, LTD., Metals Division, is to establish the first plant in Europe for the production of wrought beryllium. The plant is designed to produce semi-fabricated forms of the metal, such as rod, tube and plate, and finished machined parts. Its first task will be the execution of a production scale contract placed with I.C.I. by the United Kingdom Atomic Energy Authority (Industrial Group) as part of a nuclear development project. Subsequent spare capacity may find additional outlets for the metal, as for example in the aircraft industry.

Interest in beryllium as a nuclear engineering material has been intensified by the need for a metal which will perform satisfactorily in the higher operating temperatures envisaged in gas-cooled reactors. For the present programme of British reactors, operating at temperatures up to about 470° C., special magnesium alloy materials are used for sheathing the nuclear fuel. For the higher temperatures needed to obtain increased thermal efficiency, materials with greater strength at these temperatures must be used, and the most promising of these is beryllium.

This metal, which has a melting point of 1,280° C., is light in weight, has good mechanical properties and good corrosion resistance to carbon dioxide at elevated temperatures. In addition, beryllium has by far the lowest neutron absorption cross-section of any of the possible constructional metals. For this reason, the Industrial Group, U.K.A.E.A., intends to use beryllium fuel cans in its Advanced Gas-cooled Reactor, in which fuel element surface temperatures as high as 600° C. are planned.

The handling and fabrication of beryllium involve specialised techniques to overcome difficulties arising from its particular metallurgical characteristics and from the toxic properties of the metal in certain compounds and forms. Thanks to considerable research which has been carried out into the safe handling of beryllium products by the U.K.A.E.A., stringent standards of operation have been evolved and codified, and the I.C.I. plant will incorporate all the special features which have been found necessary for this purpose.

Some unusual features are involved in the manufacture of wrought forms of beryllium. The metal, which is received as flake or as small beads, is melted under vacuum in induction furnaces to produce an ingot. This is really a refining process : the cast ingot, having a large grain size and very poor workability, cannot be rolled or extruded directly in the same way as conventional metals are. It has to be made into fine powder which is then heated and compacted under vacuum to produce the various shapes required for further processing by conventional plant.

I.C.I. has been entrusted with this task following its already considerable contributions to the development of nuclear metallurgy. In the very early days, it solved problems connected with the extrusion of uranium and undertook the production of porous barriers for diffusion membranes in uranium isotope separation plant. Much of the early work in devising suitable forms of sheathing (or canning) for nuclear fuels was done by the Metals Division in conjunction with the Authority. I.C.I. aluminium cans are in use in many of the experimental reactors at Harwell and elsewhere, and the Division has manufactured and supplied prototype cans in magnesium and zirconium alloys to all the Consortia in this country and to official bodies aborad.

Marston Excelsior, Ltd. (an I.C.I. subsidiary) was one of the first commercial undertakings to be associated with the U.K.A.E.A. in the assembly of research reactor fuel elements containing enriched uranium, and has supplied ancillary coolers and brazed assemblies for the burst cartridge monitoring system at Calder Hall. Berkeley and Bradwell-on-Sea power stations will incorporate nearly 400 miles of I.C.I. Integron steel tubing in their heat exchangers.

The Metals Division has for many years undertaken special research and development on the "newer" metals. Titanium and zirconium have already left this class and are in commercial production by I.C.I. Work is still proceeding on other metals, including vanadium, tantalum, niobium and beryllium, the last of which is now planned to be in production at the end of next year.

The potential uses of beryllium are not confined entirely to the field of nuclear engineering, and there is considerable long-term interest in the metal among aircraft and missile designers. Its very low density and high tensile strength make it a promising material for aircraft skinning. It is, in fact, reported that beryllium is being used in this way in North American Aviation's latest research aircraft X-15, designed to fly at speeds up to Mach 7. From the viewpoint of the engineering designer, the metal's most attractive property is its high strength/weight ratio ; it has a density little more than half that of aluminium and a stiffness four times as great.

Course on New Metals

ORGANISED by the Department of Chemical Technology, a special course on "New Metals and High Temperature Materials" will be held at Bradford Institute of Technology on successive Wednesday evenings from October 15th to December 10th, 1958, at 7 p.m. The course is primarily designed for metallurgists and will deal with many of the materials likely to be of interest in the nuclear energy field, as well as titanium and its alloys and high purity silicon and germanium, which have applications in the electronics field.

The fee for the course is £2 5s. 0d. Further particulars and form of registration can be obtained from the Registrar, Institute of Technology, Bradford, 7. Telephone : Bradford 28837.

N.C.L. Open Days

THE work in progress at the National Chemical Laboratory (formerly the Chemical Research Laboratory), Teddington, may be seen during the Open Days to be held on Tuesday and Wednesday, October 21st and 22nd, 1958. Applications from firms for invitations to the morning and afternoon sessions on these days should be sent to the Director not later than September 20th. Firms already on the mailing list for invitations need not re-apply.

Change of Address

As from the beginning of this month, the address of the Climax Molybdenum Company of Europe, Ltd., will be 2 Cavendish Place, London, W.1. Telephone : MUSeum 8818.

Metallic Heating Element Materials for High Temperature Furnaces

By R. Kieffer and F. Benesovsky

*Metallwerk Plansee G.m.b.H., Reutte, Tyrol, Austria**

The authors report on the physical properties of metals for high temperature heating elements and collate in tables the behaviour of molybdenum, tungsten and tantalum towards various atmospheres and the ceramic structural parts of furnaces. A number of examples are given of the practical layout of these materials in high temperature furnaces.

THE many and varied electric furnaces in industry need resistance materials for the conversion of electrical energy into heat. For the temperature range up to about 1,300° C., the materials used almost exclusively are metallic alloys having high electrical resistance and excellent scale stability, such as Ni-Cr, Fe-Ni-Cr, Fe-Cr-Al and Fe-Co-Cr-Al. In the form of wires, ribbons and sheets, they are fabricated into heating elements of many kinds.

At the present time, however, there is a demand—not only for research, but also for industrial purposes—for electric furnaces with working temperatures higher than 1,300° C. Examples include, sintering furnaces in powder metallurgy, heat treatment furnaces for high-melting alloys, kilns for firing ceramics, etc. For such purposes we now possess suitable metallic and non-metallic materials for heating elements. The non-metallic types based on silicon carbide (Silit, Globar rods, etc.), and carbon (carbon or graphite tubes and rods), which permit working temperatures up to 1,450° C., and some even over 2,000° C., will not be discussed here. Platinum and platinum alloys are now used in small and medium-sized laboratory furnaces working at temperatures up 1,700° C. Owing to high cost, relatively high vapour pressure at high temperature, and reactivity towards certain impurities such as silicon, the metals of the platinum group are practically out of the question for larger industrial furnaces. We propose, therefore, to deal only with the following metallic materials for high temperature furnaces—molybdenum, tungsten and tantalum.

As already pointed out, the main requirements are high electrical resistance and stability towards the furnace atmosphere, combined with satisfactory mechanical properties. Let us admit at once that in metallic heating element materials for the highest temperatures, not all these requirements can be fulfilled simultaneously. The metals mentioned are good electrical conductors, though, of course, as in other pure metals, the resistance rises sharply with temperature (Fig. 1). For this reason, the use of continuous or fine-step regulating transformers is generally indispensable.

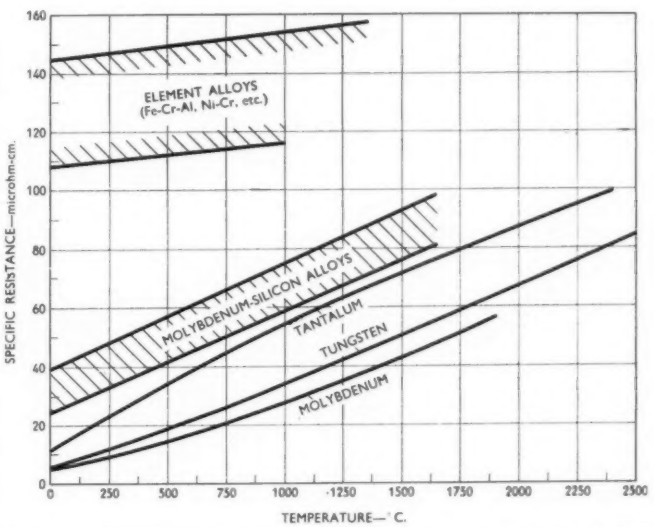

Fig. 1.—Temperature dependence of electrical resistance of heating element materials for high temperature furnaces compared with ordinary heating element alloys.

Heating must take place in protective gas atmospheres or in vacuum, and the mechanical and chemical properties do not always permit the designs of element formerly employed. All these circumstances render the materials in question suitable for certain applications and types of furnace only, though naturally some latitude is possible.

Another point to be emphasised is that many furnace elements for high temperature work, such as radiation plates, suspension hooks for heating elements, crucibles, boats, etc., are best made of metals with a high melting point.

Before we enter into details of the materials and their range of application, or of new developments, let us first consider the thermal and electrical properties illustrated in Table I, and the chemical properties in Tables II and III, especially the behaviour towards furnace atmospheres and structural materials in contact with the heating elements. Since the life at high temperatures under otherwise favourable conditions is determined chiefly by evaporation losses, Table IV, which is based on the evaporation rate values from Table I, sets out

* Agreements in this field have recently been concluded between Metallwerk Plansee and The General Electric Co., Ltd. A note regarding this will be found on page 144.

TABLE I.—PROPERTIES OF HIGH TEMPERATURE HEATING ELEMENT MATERIALS

Property	Unit of Measurement	Molybdenum	Tungsten	Tantalum
Melting Point	°C.	2,360	3,410	3,030
Specific Heat at 20° C.	cal/g/° C.	0·065	0·033	0·036
Coefficient of Expansion at 20° C.	$\alpha \times 10^6$	5·3	4·4	6·6
Thermal Conductivity at 20° C.	cal/cm²/cm/° C/sec	0·37	0·31	0·13
Rate of Evaporation at 1,530° C.	mg/sq. cm./hr.	$3·1 \times 10^{-4}$	$1·3 \times 10^{-10}$	
1,730° C.		$3·6 \times 10^{-2}$	$5·3 \times 10^{-5}$	$5·9 \times 10^{-2}$
1,930° C.		180	$7·5 \times 10^{-3}$	$3·5 \times 10^{-1}$
2,130° C.		too high for	$4·6 \times 10^{-4}$	$1·1 \times 10^{-2}$
2,330° C.		technical	$1·4 \times 10^{-2}$	2×10^{-1}
2,530° C.		purposes	$2·7 \times 10^{-1}$	2·5
Deformability		very good	good	excellent
Specific Electrical Resistance at 20° C.	microhm-cm.	5	5·5	12·5
1,000° C.		27	33	54
1,500° C.		45	50	72
2,000° C.		60	66	87
Surface Load Capacity at Temperatures <1,800° C in Continuous Operation	watt/sq. cm.	10–20	10–20	10–20
Temperatures >1,800° C. in Short Operation.		20–40	20–40	20–40

the maximum operating temperatures permissible for refractory metals from the point of view of material erosion[1]. The data as to chemical stability at high temperatures are to be taken with reserve as indicatory only, seeing that impurities in the protective gases (e.g. water vapour in hydrogen; nitrogen and oxygen in technically pure inert gases; gas residues in vacuum vessels) or impurities in ceramics (iron oxide, alkalies, silica in the pure oxides, etc.) may bring down the temperatures quoted by several hundred degrees.

Molybdenum

Following the fundamental developments in producing molybdenum and tungsten in the years after 1920, molybdenum was introduced into industrial furnaces of all kinds after about 1930, and increasingly from 1940. It proved completely successful,[2-4] and a great number of high temperature furnaces are in continual use today in the most varied industries.[5-7]

According to Kieffer and Krall,[2] three fundamental conditions were recognised as essential for practical success in building industrial molybdenum furnaces :—

(1) The use of wire of large cross-section with low voltage across the elements.

(2) Avoiding as far as possible any contact of the heating element with ceramic furnace parts.

(3) Development of suitable, mostly water-cooled, terminals for the heating elements.

The thin wires and ribbons formerly used on mains voltage always suffered the disadvantage that as the cross section became reduced by material wastage, local concentration of current led to destruction of the element. With larger cross sections, slight reductions can occur without serious effect.

Because of reaction between molybdenum and ceramic furnace parts at very high temperatures,[8,9] destruction of the element is very common. By allowing the elements to hang freely, or by supporting them at points only on suitable intermediary materials (e.g. Al_2O_3 up to 1,700° C., molybdenum hooks up to 2,000° C.) this damage through reaction can be avoided to a large extent. For temperatures above 2,000° C., the only element assemblies which have a satisfactory life are those without ceramics and, particularly in vacuum furnaces, radiation plates take the place of the classical ceramic insulations.

The well-known difficulties encountered at heating element connections are especially serious in high temperature furnaces. The contact resistances always present at the terminals give rise to heating at these points, which always increases as the temperature of the element increases. These difficulties were completely overcome by the development of water-cooled copper terminals, with the terminal or contact parts consisting of molybdenum or tantalum. This method of supplying current at the terminals resembles very closely the design of the current leads in molybdenum, tungsten and tantalum sintering bells.

The high melting point of molybdenum (about 2,600° C.) permits continuous operating temperatures of up to 1,900° C.—only then does the evaporation become

TABLE II.—STABILITY OF HIGH TEMPERATURE HEATING ELEMENT MATERIALS TOWARDS OXIDES AND FURNACE PARTS

Material	Molybdenum	Tungsten	Tantalum
Graphite	Strong carbide formation beyond 1,200° C.	Strong carbide formation beyond 1,400° C.	Strong carbide formation beyond 1,000° C.
Al_2O_3	Up to 1,900° C.	Up to 1,900° C.	Up to 1,900° C.
BeO	Up to 1,900° C.*	Up to 2,000° C.*	Up to 1,600° C.
MgO	Up to 1,800° C.*	Up to 2,000° C.* (Strong magnesia evaporation).	Up to 1,800° C.
ZrO_2	Up to 1,900° C.* (Strong molybdenum evaporation).	Up to 1,600° C.*	Up to 1,600° C.
ThO_2	Up to 1,900° C.*	Up to 2,200° C.*	Up to 1,900° C.
Sillimanite	Up to about 1,700° C.	Up to about 1,700° C.	Up to about 1,600° C.
Firebrick	Up to about 1,200° C.	Up to about 1,200° C.	Up to about 1,200° C.
Magnesite Brick	Up to about 1,600° C.	Up to about 1,600° C.	Up to about 1,500° C.

* In vacuum of 10^{-4} Torr; under protective gas about 100–200° C. lower temperatures.

TABLE III.—BEHAVIOUR OF HIGH TEMPERATURE HEATING ELEMENT MATERIALS TOWARDS FURNACE ATMOSPHERES

Atmosphere		Molybdenum	Tungsten	Tantalum
Air or Gases Containing Oxygen		Incipient oxidation beyond 400—500° C.; strong evaporation above 800° C.	Incipient oxidation beyond 500° C.; strong evaporation above 1,200° C.	Oxidation and nitride formation above 500° C.
Hydrogen	Dry (<0·5g. of water per cu.m.)	Stable up to melting point.	Stable up to melting point.	Hydride formation at 400—800° C.; beyond that, stable up to melting point, surface oxidation.
	Wet (<20g. of water per cu.m.)	Stable up to 1,400° C.; beyond that growth of metal needles on surface, with material wastage.	Stable up to 1,400° C.; beyond that growth of metal needles at surface, with material wastage.	Hydride formation and strong oxidation beyond 450° C.
Cracked Ammonia (dry)		Stable up to melting point.	Stable up to melting point.	Nitride and hydride formation above 400° C.; at higher temperatures thorough nitrification.
Partially Burnt Ammonia (dry)		Stable up to melting point.	Stable up to melting point.	Nitride and hydride formation above 400° C.; at higher temperatures thorough nitrification.
Partially Burnt Illuminating Gas, Generator Gas, etc.		Stable up to 1,300° C.; surface carbonisation above 1,300° C.	Stable up to 1,400° C.; surface carbonisation above 1,300° C.	Nitride, carbide and hydride formation; becomes brittle.
Inert Gas (argon, helium)		Stable up to melting point.	Stable up to melting point.	Stable up to melting point.
Vacuum	$<10^{-2}$ Torr	Stable up to 1,700° C.	Stable up to 2,000° C.	Becomes brittle through getter action on gas residues.
	$<10^{-4}$ Torr	Strong evaporation above 1,800° C.	Strong evaporation above 2,400° C.	Strong evaporation above 2,200° C.

at all serious (Table I). Molybdenum wires and ribbons are easily fabricated to heating elements of all kinds. Since there is rapid oxidation on heating above 600° C. in air—the MoO_3 formed being readily volatile—molybdenum can only be heated in reducing atmospheres such as hydrogen, cracked ammonia, partially burnt town's gas, or inert gas. Of course, a vacuum of less than 10^{-2} Torr can also be used.[6] If, however, there is a poor vacuum due to gas residues (air, carbon dioxide, water vapour) there may be oxidation, and the heating element is soon destroyed.

In high vacuum ($<10^{-4}$ Torr) account must be taken of the evaporation of molybdenum, which becomes considerable above 1,600°–1,700° C. It is better, therefore, to use tantalum or tungsten in high vacuum furnaces working above 1,700° C.

The marked effect of temperature upon the electrical resistance of molybdenum (see Table I), makes it necessary for molybdenum heated furnaces to have control transformers which can be combined with temperature control devices. The chief application of molybdenum heating elements is in furnaces with a reducing or inert protective gas, and in vacuum sintering furnaces for powder metallurgy, also muffle furnaces for hard soldering and annealing, and certain smelting furnaces, e.g. for copper, uranium, etc.[5-7]

TABLE IV.—MELTING POINTS AND HIGHEST WORKING TEMPERATURES FOR HIGH MELTING METALS AND IN WHICH AFTER 100 HOURS THE EVAPORATION LOSS DOES NOT EXCEED 1%.

Metal	Melting Point (° C.)	Highest Working Temperature (° C.)
Tungsten	3,410	2,560
Tantalum	3,030	2,400
Rhenium	3,180	2,380
Niobium	2,420	2,230
Molybdenum	2,630	1,910
Platinum	1,773	1,600

Fig. 2*a* shows a view from above of an element cage consisting of bundled molybdenum wires and molybdenum sheets in a furnace for working at a vacuum of 10^{-4} Torr and 1,400° C. A schematic section appears in Fig. 2*b*. Fig. 3*a* shows a row of large muffle furnaces for continuous working at 1,700° C. overall, i.e. 1,800–

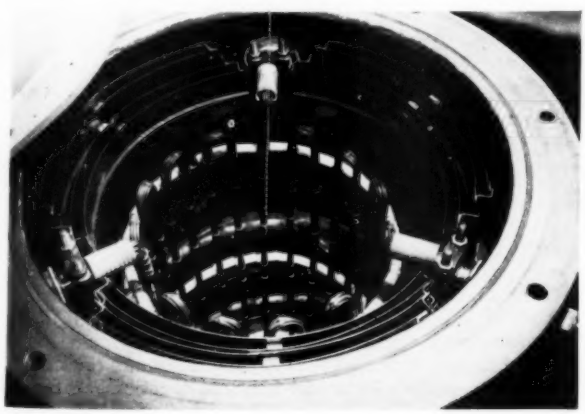

Fig. 2a.—High vacuum sintering furnace with cage-form molybdenum heating element. The working temperature is 1,400° C., the rating 40 kW., and the vacuum $<10^{-2}$ Torr.

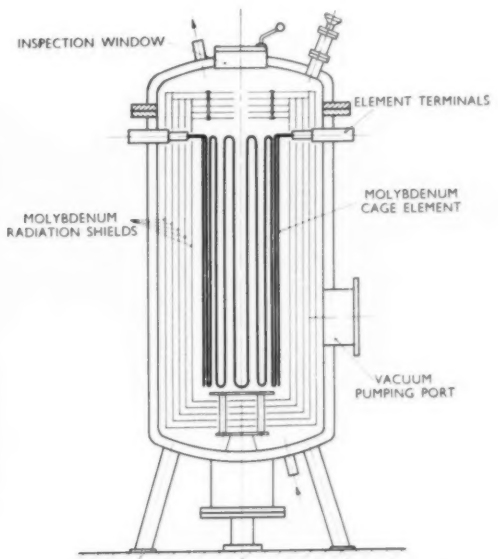

Fig. 2b.—Section through furnace shown in Fig. 2a.

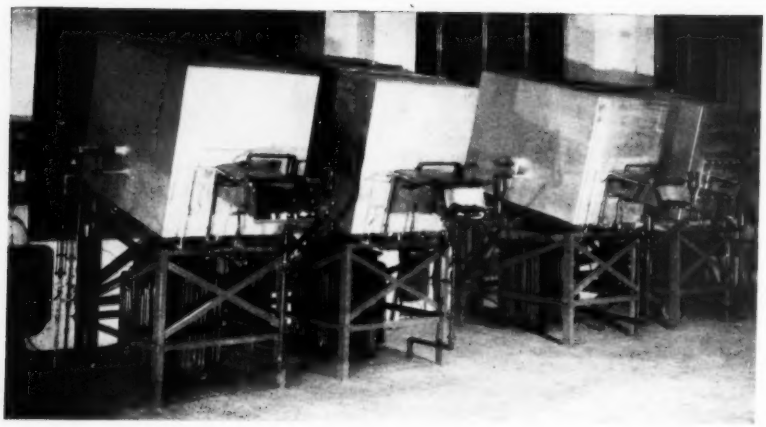

Fig. 3a.—Group of high temperature muffle furnaces with molybdenum heating elements. The working temperature is 1,700° C., the rating 40 kW., and the protective gas hydrogen.

Fig. 3b.—Section through furnace shown in Fig. 3a.

1,900° C. at the heating element, with fairly dry hydrogen atmospheres, the section being as in Fig. 3*b*. In these furnaces the lining in the high temperature zone needs to be of special materials. Up to 1,800° C., bricks of high magnesia and high alumina contents have served well (> 90% MgO and > 90% Al_2O_3). In some cases, however, pure alumina bricks (> 99% Al_2O_3) are preferred.

Molybdenum furnaces in which the heating wire is wound on sintered alumina tubes work continuously at 1,500°–1,600° C., particularly for sintering hard metal; more recently they have been used at 1,800° C. for firing ceramics.[10]

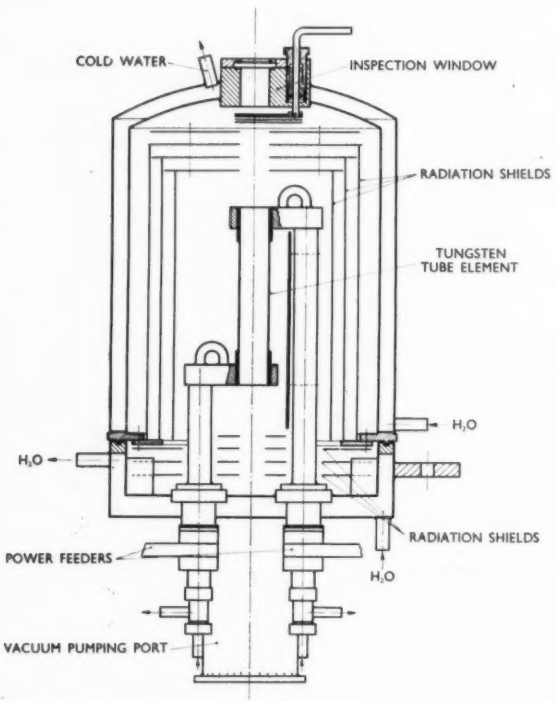

Fig. 4.—Vertical tungsten tube furnace for temperatures up to 2,500° C., working under protective gas or high vacuum.

Many remarks in this section apply equally to the sister metal, tungsten.

Tungsten

Tungsten, with a melting point of about 3,400° C., provides the heating element for the highest working temperatures. For this reason also, tungsten is employed on the widest scale for incandescent lamp filament coils and for anodes in X-ray tubes.[11] In most applications, the working temperature of the metal may reach 2,000°C., and it is even possible to reach 2,500° C. in furnaces with tungsten heating elements, provided that no contact is permitted between the metal and ceramics; i.e. in so-called "ceramic-free construction". Since tungsten is much more difficult to work than molybdenum or tantalum, it is used mostly in the form of round rods, sheet strips, or—better still—roughly swaged tubes, as heating elements. Owing to the difficulty of insulation at such high temperatures, most of the furnace units are

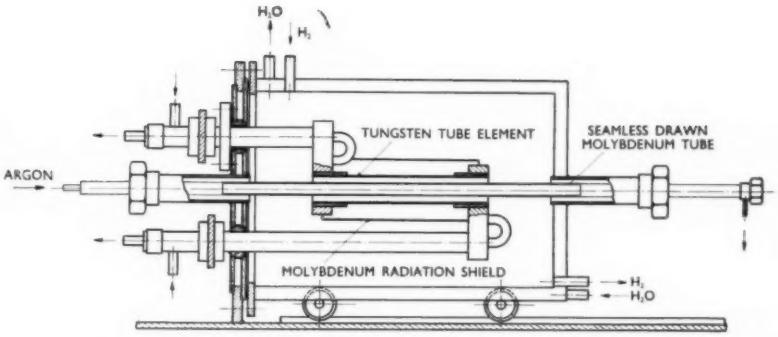

Fig. 5.—Horizontal tungsten tube furnace with molybdenum tube inserted for working at temperatures up to 2,000° C., under inert gas.

small and for laboratory use, but furnaces of this kind have been built with cage-like elements and terminal values of over 200 kVA. Tungsten, like molybdenum, can be used only in a reducing or inert protective gas, or a vacuum of less than 10^{-2} Torr. The evaporation rate is very low, even at very high temperatures (see Table I), and brittleness can be kept down by additives which prevent recrystallization.

Since even thorium oxide fails to insulate above 2,200° C., a good method of construction for a tube furnace is to mount the tungsten tube between two water-cooled copper clamps and enclose the whole arrangement in a water-cooled tank, this being filled with protective gas or evacuated (Fig. 4). For prevention of radiation, several molybdenum or tantalum sheet screens are placed round the heating tube. If one wishes to ignite samples at 2,000°–2,400° C., e.g. in purified inert gas, one can insert a seamless drawn molybdenum tube in the tungsten heating tube, both being protected on the outside by hydrogen, whereas inside, where the sample to be ignited is situated, a gas such as argon can be used as neutral protection.[12] This arrangement is shown schematically in Fig. 5. In the furnace types seen in Figs. 4 and 5, in spite of the intensive cooling at the copper terminals, prolonged operation at the highest temperatures leads to difficulties. These can be avoided by the use of tantalum terminals (Fig. 6).[13] Such furnaces with tantalum terminals can, of course, be used only with high vacuum or inert gas. Furthermore, furnaces with tungsten heating elements must be provided with a control transformer, owing to the variation of conductivity with temperature.

By applying induction heating, the contact problems can, of course, be circumvented. Several designs for laboratory furnaces have been evolved. Fig. 7 shows schematically a vacuum quenching furnace in which the hot chamber of tungsten or tantalum is heated by induction from the outside. A zirconia tube with zirconia powder serves for insulation.

Tantalum

Tantalum, with its high melting point of about 3,030° C., can likewise be heated to a high temperature, the evaporation rate being low (less than that of

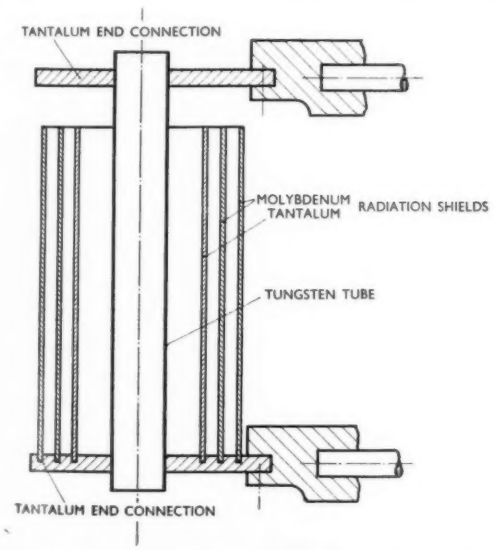

Fig. 6.—Arrangement of tungsten heating tube with tantalum terminals in a high temperature furnace. (Everly and Lambertson).

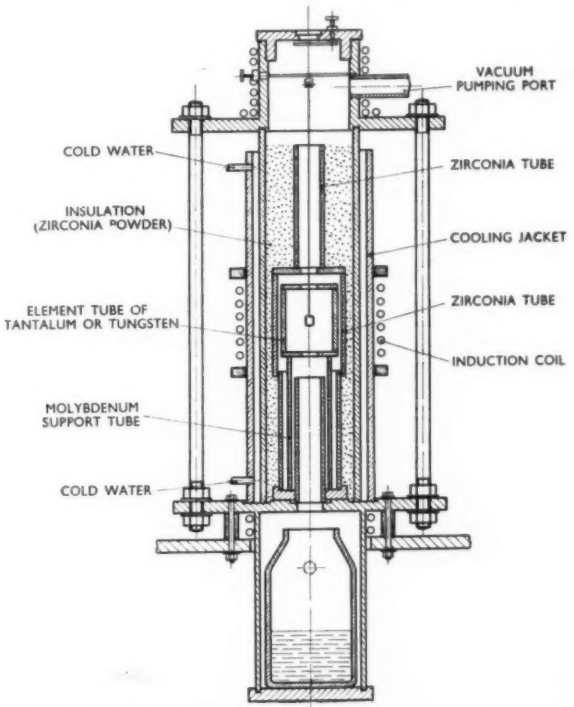

Fig. 7.—Vacuum induction furnace with heating chamber of tungsten or tantalum. (Everly and Lambertson).

molybdenum, greater than that of tungsten (Table I)). Niobium (see Table IV) has high temperature properties about as good as tantalum. At present, its high cost is against its use for heating elements. In the future, this metal and its alloys with others of high-melting point, will become more important.[14] Tantalum ingots annealed in vacuum are extraordinarily ductile, and coils and tubular heating elements of varied form can, therefore, be easily made. It is true that these can only be heated in vacuum $<10^{-4}$ Torr or in inert gas. In hydrogen, oxygen, nitrogen or carbon-containing atmospheres, gas absorption and chemical reaction begin with the formation of nitride, carbide, oxide or hydride, causing immediate brittleness, which cannot be removed—or at least only partially. Hydride formation is reversible, so that tantalum sheet rendered brittle by hydrogen can be softened again by heating in high vacuum. To a certain extent, even tantalum oxide can be removed by dissociation or, owing to its high vapour pressure, can be pumped out at high temperature.

Even after long heating, and in spite of recrystallization, no brittleness occurs with tantalum as with molybdenum and tungsten. Thus, tantalum is a typical heating element material for high vacuum furnaces in the region of 2,200° C. Fig. 8 shows schematically the heating element rig of such a furnace. Control transformers are required also for tantalum heating elements.

Owing to its pronounced ductility and getter activity, tantalum is specially useful for screening plates and ignition cells for sensitive objects undergoing annealing. The application of tantalum in terminals of tungsten tube furnaces has already been mentioned.

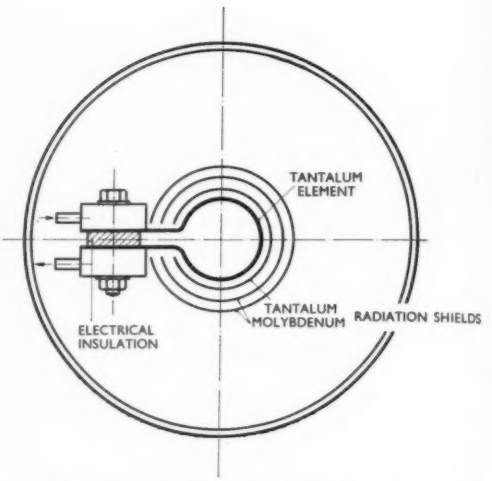

Fig. 8.—Arrangement of heating element rig in a tantalum sheet high vacuum furnace.

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Castings in Pickle

IN order to provide facilities for the acid pickling of steel castings of wide variety and weight, the David Brown Foundries Division at Penistone has installed tanks capable of holding even the largest of their products. Employed in conjunction with hand fettling, pickling of castings in hydrochloric or sulphuric acid ensures that all foreign matter is removed from the metal, at the same time revealing defects, such as cracks, if these exist. It is anticipated that the largest castings to which the pickling process will need to be applied will be the half turbine casings, weighing up to eight tons, for which orders are currently on hand for conventional and atomic power stations.

Casting being lowered into empty tank whilst pickling proceeds in the adjacent tank.

Two identical tanks have been built, together with a neutralising sump. A two-way reversible pump serves both tanks and is capable of effecting complete transfer of the liquid in five minutes. After lowering the casting (or castings) into the empty tank, the slinging chains are removed, and acid is then transferred from the other tank.

By means of heating elements, the acid solution (about 10% strength) is maintained at a temperature of about 60° C., at which heat pickling goes on for about two hours. By loading the second tank in the meantime, a continuous flow of work is ensured. Only very infrequently is it necessary to dispose of the acid, this being effected after a neutralising lime solution has been added.

Deformation Mechanisms in Magnesium and Some Magnesium-Aluminium Alloys

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Based on a literature survey made as part of a general programme covering the properties of potential alloys for canning nuclear fuels in gas-cooled reactors, this paper discusses the modes of deformation of magnesium and magnesium-aluminium alloys and considers the formation of intergranular holes. It is suggested that more than one mechanism of hole formation is operative.

THE use of a magnesium alloy as a canning material for gas-cooled thermal reactors has centred interest on the deformation characteristics of this metal and its alloys. The important feature in applications of this type is the requirement that the can should remain leak tight during irradiation. This implies that the selected alloy must have good ductility over a wide range of temperatures and strain rates. Exceptional creep resistance is not essential. This paper is based on a literature survey which was made as part of a general programme covering the properties of potential canning alloys.

Modes of Deformation

Magnesium is a hexagonal close-packed metal with an axial ratio, c/a, equal to 1·624. It deforms by twinning, slip or grain boundary flow according to the conditions, and cell structures develop over a restricted temperature range.

In common with other hexagonal metals, the twinning plane for magnesium is $(10\bar{1}2)$. The incidence of twinning decreases with increase of temperature, and is virtually absent at temperatures above 300° C.[1] The work of Roberts[2] shows that twinning contributes almost exclusively to primary creep, the actual contribution being governed by orientation relationships.[2, 3]

The accepted mechanisms of deformation of magnesium at room temperature are by slip on (0001) planes in [1120] directions. Barrett[4, 5] suggests that non-basal slip on the $(10\bar{1}1)$ planes is also possible at room temperature. At higher temperatures other slip mechanisms become operative. Work by Bakarian and Mathewson,[6] Chaudhuri, Grant and Norton[7] and Roberts[2] has shown that slip can occur on $(10\bar{1}1)$ and $(10\bar{1}2)$ planes at temperatures above 225° C., whilst Chaudhuri, Chang and Grant[8] have concluded that a co-operative form of slip is possible on $(10\bar{1}0)$ and $(10\bar{1}1)$ planes of $\langle 1120 \rangle$ zones at temperatures of 260–370° C. The latter workers imply that low strain rates favour the co-operative form of slip, and that basal slip is most prevalent under high strain rate conditions.

The variations in slip band width and spacing which occur with changes of temperature and, or, grain size are of interest. Grant, Servi and Chaudhuri[9] have studied the effects of grain size on slip and grain boundary sliding in magnesium deformed at 260° C. They found that, for a given grain size, the slip band spacing increased with decrease of stress until the spacing was of the order of half the grain diameter. In both magnesium and aluminium of mixed fine and large grain sizes, the coarse grains showed slip and the fine grains showed evidence of grain boundary sliding. Suiter and Wood[1] report that above 200° C. the incidence of slip is markedly reduced in magnesium, and that much of the deformation occurs by grain boundary movements and cell formation. However, recent work on a wide range of metals by McLean and Farmer[10] suggests that grain boundary flow does not occur independently of slip, and these workers have proposed a mechanism whereby grain boundary sliding is controlled by crystallographic slip. Martin Herman and Brown[11] have reached a similar conclusion in work on β-brass.

Cell formation has been observed in many metals, and there are two schools of thought as to the origin of these cells. Wood *et al.* consider sub-grain formation to be a mechanism of deformation which is operative under certain conditions, in the same way that slip is a mechanism of deformation under other conditions. The other school of thought, followed by Grant *et al.*,[7, 9] Greenough *et al.*,[12] and Wyon and Crussard,[13] is that cell formation results from a stress-accelerated polygonisation process caused by non-homogeneous distortion. Calnan and Burns,[14] Ramsay,[15] and Chaudhuri, Grant and Norton[7] have noticed in the case of aluminium, zinc, and magnesium (especially in coarse grained aggregates) that the breakdown of the metals into cells is marked in the grain boundary regions. Wyon and Crussard[13] claim that polygonisation can be so pronounced in the grain boundaries that it actually leads to recrystallisation.

Suiter and Wood[1] have suggested a mechanism for the formation of cell structures. This depends on relative movements of the grain boundaries causing rumpling and twisting of the structure. Dislocation movements relieve the strain associated with the deformation and lead to the formation of sub-boundaries which develop into the observed cell structures. Suiter and Wood have observed this effect in magnesium at temperatures above 200° C., where they report that slip ceases to be an operative mechanism and strain hardening is almost absent.

In constant strain rate tests at 0·14% per hour on a magnesium–0·8% aluminium–0·005% beryllium alloy, the author has observed extensive cell formation at temperatures between 100–300° C. The structures observed were well-defined and their response to polarised

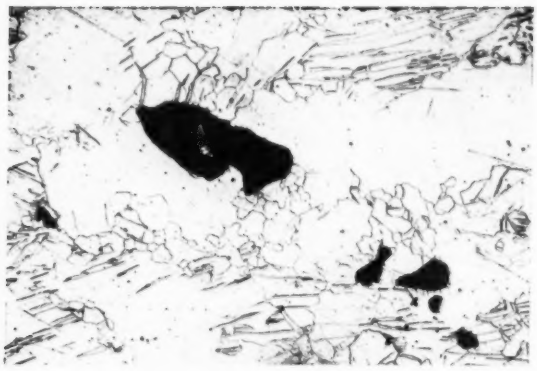


Fig. 1.—Fine grain structure developed in original boundaries during test at 200° C. and 0·14% per hour strain rate. × 100

light suggests that the cells are, in fact, small fully recrystallised grains. An example is shown in Fig. 1. In a test at 175° C., the author found that slip was quite general through the specimen, although rather variable in extent, but did not detect any grain boundary movements. Fig. 2 shows a typical area within a grain deforming under at least two slip systems. Fig. 3 shows grains with single slip systems visible, and also rumpling adjacent to the grain boundaries.

In magnesium, where there are relatively few deformation systems compared with cubic metals, there can be expected to be pronounced differences in the amount of slip and twinning occurring in different grains. Extensive deformation in one grain will produce strain in the vicinity of its own grain boundary, and in adjacent unslipped or less slipped grains, which must be accommodated in some way if the metal is to retain its continuity. At low temperatures grain boundary movement is not observed, and the strain must be accommodated by lattice bending in the vicinity of the grain boundaries. This type of distortion can produce large numbers of dislocations, and under suitable conditions of temperature these are able to migrate, leading to polygonisation and recrystallisation processes.

As the temperature is increased, the amount of visible slip decreases and grain boundary movements can occur. Hence the strain to be accommodated by lattice bending in the vicinity of the grain boundaries will decrease with increase of temperature. Thus, an intermediate range of temperature may be expected in which fine cell structures are particularly well developed. This temperature range will be dependent on strain rate and, as the strain rate is decreased, there will be more time for the recrystallisation processes to occur.

This means that the cell structures should develop at lower temperatures as the strain rate is decreased. Similarly, the effect may be expected to occur at lower temperatures as the grain size is decreased, and to be less pronounced due to the enhanced ductility of fine grain material.

Mechanisms of Nucleation and Growth of Holes

The various deformation processes enumerated above occur simultaneously with the formation of intergranular holes, and may be important in determining their shape and frequency of occurrence.

Perhaps the simplest theory of nucleation of holes is that which considers as responsible the stress build-up at triple points due to boundary movements. In this theory, unless the grain boundary movements can be accommodated by deformation within the grains, intercrystalline cracking will occur commencing at the triple points. Holes develop in magnesium and its alloys at triple points and also along the boundaries away from triple points. Thus, from the latter fact, it seems that holes are not always the result of stress concentration.

Greenwood[16] proposed in a qualitative way that holes are formed by aggregation of vacancies. Machlin[17] investigated this problem theoretically, and concluded that nucleation of holes by condensation of vacancies under creep rupture conditions is highly improbable, but heterogeneous nucleation is possible at imperfections or impurities. Machlin was able to predict from his theory that the product of rupture life and steady state creep rate for pre-annealed metals and single-phase alloys is an approximately invariant quantity for a given type of structure. He also predicted that cold work should

Fig. 2.—Two slip systems operating within a grain of polycrystalline magnesium-aluminium alloy strained at 0·14% per hour at 175° C. × 200

reduce the elongation at fracture. Both predictions were confirmed and Machlin suggested certain critical experiments to check the basic assumptions of his theory. The first experiment was to stop a test in the transcrystalline stage of rupture before failure, when, according to Machlin, it should be possible to observe spherical holes within the grains. This has been done several times by the author with magnesium-aluminium alloys, and no holes have been found within the grains. In compression creep tests on a magnesium–0·8% aluminium alloy producing 5% strain, the author found no holes in the grain boundaries, contrary to the expectations of the second experimental test proposed by Machlin. A tensile strain of 5% would produce holes at comparable stresses and temperatures.

The theory of creep and rupture evolved by Crussard and Friedel[18] considers vacancies to be the controlling factor in hole formation. The excess vacancies required can be generated by :—

(1) Dislocations moving in intersecting slip planes crossing and producing rows of vacancies or interstitials, due to their screw components.

(2) Dislocations climbing over obstacles, precipitates,

sessile dislocations, etc. This process may occur through absorption or emission of vacancies. If the "climb" is rapid there can be a local temporary excess of vacancies.

Crussard explains the clustering of vacancies in the grain boundaries in terms of a repulsive elastic interaction between vacancies (unless they are very close together) in the crystal lattice, and this interaction is reduced, or even eliminated, in the grain boundaries. Some of the vacancies generated near grain boundaries by the processes described above are attracted to the "compressed" side of dislocations, the movement of which in the grain boundary has been blocked, and which are unable to climb out of the boundary because their Burgers vectors lie either in the boundaries or at very small angles to them. In this way the form of nuclei and the mode of growth are both defined.

Gifkins[19] has proposed yet another mechanism of hole formation in grain boundaries. In this case crystallographic slip is assumed to develop jogs in the grain boundary. These jogs are then opened up by grain boundary flow if they are suitably oriented relative to the direction of flow. The holes, once formed, are assumed to grow by stress concentration. Jogs which would oppose grain boundary flow may be removed by boundary migration. If this theory is correct, then there should be an orientation dependence for the formation of cavities. Another theory using the concept of grain boundary jogs has been advanced by Chen and Machlin.[20] In this theory it is considered that grain boundary sliding sets up stresses at jogs in the grain boundaries. These stresses build up until they cause fracture at the jogs, and grain boundary sliding then opens the fracture to form a hole. The essential difference between the two theories is that Gifkins considers that the jogs are formed as a result of deformation, whilst Chen and Machlin consider that the jogs are present naturally in the grain boundaries. Both theories depend on grain boundary sliding to develop holes, and can only be considered possible mechanisms at high temperatures. Certainly, in magnesium and low aluminium alloys, the author has not observed any grain boundary movement at 175° C.

Brinkman[21] has considered the mechanism of hole formation associated with the Kirkendall effect. He concluded that in the presence of a stress field, holes of effective radius greater than 0·001 cm. will grow by vacancy condensation, even if there is no excess concentration of vacancies. Brinkman described how, in regions of stress concentration, dislocations could build up and eventually produce long fissures in the crystal lattice, which rapidly become rounded as a result of surface diffusion, and which might be large enough to grow in the absence of an excess vacancy concentration.

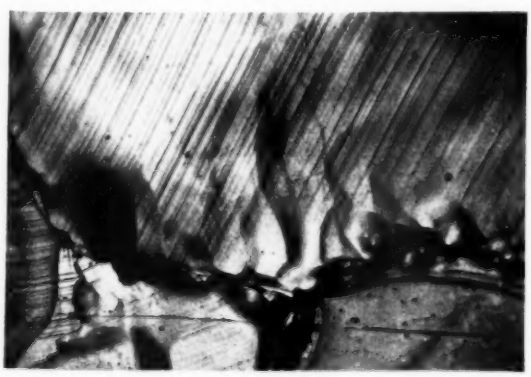


Fig. 3.—Rumpling near grain boundaries in magnesium-aluminium alloy; also single slip system operating in test at 175° C. and 0·14% per hour strain rate. × 200

Thus, in both problems, creep and diffusion, vacancy condensation alone has not been satisfactorily applied to the problem of hole formation. The theories developed have generally posulated mechanisms for the formation of hole nuclei which are dependent on blocked dislocation movements.

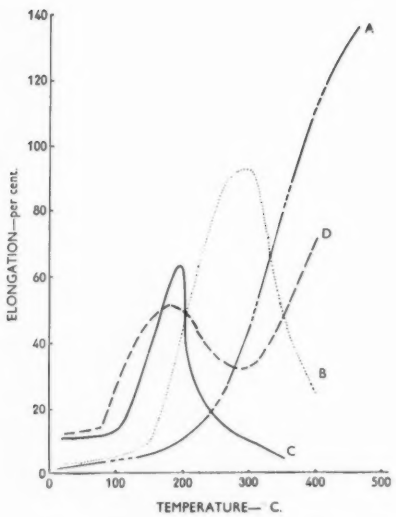
In recent work on magnesium-aluminium alloys, the author found that holes formed at all temperatures from 25° C. to 400° C., and at strain rates between 0·1% per hour and 1075% per hour. Toaz and Ripling[22] have made similar observations over a temperature range extended to — 75° C. Additionally, the shape of the holes, frequency of occurrence, and location varied. At temperatures below 150° C. the holes were in the form of long fissures, whereas at higher temperatures they were rounded. Consequently, it seems unlikely that any one mechanism can be applied to the nucleation and growth of the holes.

It is suggested that at high strain rates the mechanism of hole formation is more likely to be that of stress concentration. Under these conditions there is little time for cell formation or for vacancy diffusion. At temperatures of 100° C., or less, the form of fracture suggests a type of brittle fracture associated with a small amount of plastic strain. The effect of strain rate is not yet certain. The transition temperature at which the change from brittle to ductile fracture occurs is a function of grain size. Hauser, Landon and Dorn,[23] in work on magnesium and magnesium–2% aluminium, have studied the variation of fracture stress with temperature for material with different grain sizes. Interpolation between their results indicates a transition temperature of about 140–150° C. for a magnesium–0·8% aluminium alloy with a grain size of 0·02–0·03 in. This is in reasonable agreement[2]with the observed behaviour, in that there is a difference in the form of holes obtained at 100° C. and those obtained at 150° C. In slow strain rate tests at higher temperature, vacancy condensation may account for the growth of the observed holes and, under suitable conditions of temperature and grain size, grain boundary flow may also contribute. A feature which any successful theory must explain is the decrease in incidence of holes which appears to occur at temperatures above 400° C. In a theory based on vacancy condensation, this may be explained by assuming that the vacancies are so mobile that local concentrations of vacancies required for condensation do not exist for a sufficient period of time.

The role of surface free energy is that of a restraining force, and it is generally accepted that it will oppose the growth of holes and tend to make them spherical. Effects due to this restraint will be most marked at high temperatures, and may also contribute to the reduction in the number of holes observed at test temperatures above 400° C.

Variation of Elongation with Temperature

Greenwood and his co-workers[16] obtained interesting variations in the ductility-temperature relationship for a magnesium–0·2% lead alloy when tested under constant strain rate conditions. Similar results have



A. MAGNESIUM—0·2% LEAD ALLOY TESTED AT 1,000% PER HOUR STRAIN RATE.[18]
B. MAGNESIUM—0·2% LEAD ALLOY TESTED AT 40·0% PER HOUR STRAIN RATE.[18]
C. MAGNESIUM—0·2% LEAD ALLOY TESTED AT 0·2% PER HOUR STRAIN RATE.[18]
D. MAGNESIUM—0·8% ALUMINIUM ALLOY TESTED AT 0·14% PER HOUR STRAIN RATE.

Fig. 4.—Variation of elongation with temperature for magnesium alloys in constant strain rate tensile tests.

been obtained by the author on magnesium-aluminium alloys. Fig. 4 illustrates these effects. Greenwood and his co-workers explained the peaks in the curves in the following way.

(1) The increase in ductility at temperatures of 100–200° C. is due to the operation of slip planes in addition to the basal planes. It was suggested that the temperature at which these planes become operative is dependent on strain rate.

(2) The loss of ductility in the range 200–400° C. is attributed to the onset of hole formation in the boundaries.

The type of elongation temperature curve shown in Fig. 4 for magnesium is also exhibited by aluminium in the range 200–400° C., and is demonstrated in the work of Carraker and Hibbard.[24] In this case the effect of additional slip systems coming into operation at elevated temperatures should be less marked, as there are more slip systems normally available for deformation than in the hexagonal magnesium. However, marked substructure formation is possible in aluminium.

In the author's work, holes have been observed in all the tests, and were not confined to the zones where elongation was decreasing with increasing test temperature. The marked development of cell structures adjacent to the original grain boundaries has frequently been observed. In these tests, a very well-defined fine crystal structure developed adjacent to the original grain boundaries in the range 100–300° C. The extent of this structure varied with temperature in a similar way to the percentage elongation; i.e., from 100–180° C., the amount of fine grain structure increased, and from 180–300° C. it decreased again, and was almost entirely absent at higher temperatures. Excluding very coarse grained material, with special orientations relative to the tensile strain, fine grained metal is more ductile in creep than coarse grained metal. It is suggested that the increased ductility is due, at least in part, to the development of this fine grained material, rather than to the factors enumerated by Greenwood. A mechanism for the formation of these fine grains is suggested earlier in the section on "Modes of Deformation." The high concentration of dislocations which lead to cell formation and recrystallisation near the grain boundaries may provide vacancies also in the way described by Crussard, which at sufficiently high temperatures diffuse rapidly enough for nuclei to grow into observable holes. The frequent occurrence of holes and cell structures together is then explained.

The increase in ductility at temperatures above 280° C. is attributed to the operation of additional slip mechanisms.

Conclusions

(1) Holes form in magnesium and magnesium-aluminium alloys as a result of deformation at temperatures between 25° C. and 400° C., and at strain rates between 0·14% per hour and 1075% per hour.

(2) The variations in shape, location and number of holes suggest that more than one mechanism of hole formation and growth is operative.

(3) It is suggested that the peak in the elongation-temperature curve of magnesium and magnesium-aluminium alloys is in part due to the development of a fine grained structure adjacent to the original grain boundaries.

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Nuclear Engineering Collaboration

FOLLOWING many years of successful co-operation in the design of conventional steam raising plant, Babcock & Wilcox, Ltd., and The Babcock & Wilcox Company of America have now extended their technical collaboration into the nuclear power field. The British Company has had an experience of ten years in nuclear engineering in collaboration with the United Kingdom Atomic Energy Authority. Similarly, The Babcock & Wilcox Company became involved in the American nuclear programme over ten years ago and has co-operated closely with the United States Atomic Energy Commission on nuclear developments.

Comparison of Charpy V, Charpy U and Izod Notched Bar Tests on Steel over Transition Temperature Range

By A. W. Johnston, A.M.I.Mech.E.

Mechanical Engineering Research Laboratory, East Kilbride

A VARIETY of tests are used to assess the notch-toughness of steels for structural purposes. Test pieces for three of these tests, the Izod test, the Charpy U-notch test and the Charpy V-notch test, are described in B.S.131 : 1933. In two of these, in addition to the standard form, subsidiary standard test pieces have been devised for use where the material form necessitates a smaller test specimen.

The advantages to be derived from intercorrelation of the results of standard and subsidiary standard tests of various kinds need no emphasis, particularly as the bulk of past experience relates to test pieces of the standard forms. Considerable effort has been devoted to attempts to establish such intercorrelation, and a suggested relationship between Izod and Charpy U-notch test results was published in B.S.131. In general, however, such attempts have met with little success, and a review by Fettweis[1] suggests that this results largely from the failure to take into account the difference between cleavage and shear fracture.

An investigation comprising over 1,200 tests has been undertaken at the Mechanical Engineering Research Laboratory to compare results from the above three types of test, using both standard and subsidiary standard test pieces, over the ductile-brittle temperature ranges of six steels. The materials were three mild steels (0·07%C, 0·10%C and 0·15%C) and three alloy steels (2½% Ni-Cr, 3½% Ni-Cr and 0·4%C, 1% Ni). The notch profiles were formed by grinding, and the tests were made at temperatures ranging from −196° to 110° C. in a standard 120 ft.-lb. Izod impact testing machine and a standard 30 m.-kg. Charpy impact testing machine.

The principal conclusions which could be drawn from the results are as follows :—

(1) No simple relationship appears to exist between the results of the Izod test, the U-notch Charpy test and the V-notch Charpy test that can be applied to all six of the materials tested.

(2) The relationship between Izod and U-notch Charpy test results proposed in B.S.131 : 1933 is satisfied only by the results from the three alloy steels. A different relationship of similar form was found for the three mild steels.

(3) No simple relationship appears to exist between the absorbed energies for 10 mm. × 10 mm. test pieces and 10 mm. × 5 mm. test pieces, for any of these three tests, that will apply to all six materials.

(4) An approximate relationship of linear form was found between 10 mm. × 10 mm. and 10 mm. × 5 mm. Izod test results for four of the steels tested. For 10 mm. × 10 mm. test pieces from all the steels, the transition from ductile to brittle fracture for V-notch Charpy test pieces occurs at a higher temperature than for the U-notch test pieces. This applies also to the three mild steels when tested using 10 mm. × 5 mm. test pieces.

(5) Transition curves obtained respectively from Izod and Charpy U-notch tests extend approximately over the same range of temperature.

(6) The energies absorbed by test pieces cut from the test bars in a transverse direction are, in general, lower than those from test pieces cut in a longitudinal direction.

The full report of the work which is summarised briefly above gives detailed results and includes 38 diagrams, showing the temperature transition curves for the test materials obtained from the different tests, and indicating relationships between the results where they appear to exist.

Acknowledgment

The work described was carried out as part of the research programme of the Mechanical Engineering Research Board, and this note is published by permission of the Director of Mechanical Engineering Research, to whom application may be made for copies of the complete report.[2]

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Roto-Finish Maintenance Agreement

ROTO-FINISH, LTD., announce the introduction of a twelve months' maintenance agreement, whereby a trained service engineer will visit customers' factories once every four months to overhaul and maintain Roto-Finish equipment. This agreement will be available in the first instance for factories in the main industrial areas, but it is planned to extend the service to the whole of the United Kingdom in due course. This service is not intended to replace but is in addition to the very comprehensive free service that Roto-Finish already give to their customers.

Crofts' North American Activities

CROFTS ENGINEERS (HOLDINGS), LTD., the Yorkshire power transmission engineers, announce the opening of a subsidiary company, Crofts U.S.A., Ltd., (with headquarters in Chicago) to deal with trading activities in the U.S.A. Following closely on the recent acquisition of new and larger head office and works in Montreal and Toronto for Crofts Canada, Ltd., the new American company is a logical development of the group's policy of vigorous expansion overseas.

Mercury Patterns for Precision Castings

Mercast Process in Operation at Crawley

ABOUT three years ago, two companies of long standing in the metallurgical field—Guest, Keen and Nettlefolds Ltd., and The Telegraph Construction and Maintenance Co., Ltd.,—extended their interests to the precision casting field and formed Sankey-Telcon, Ltd. After considering the various techniques for the manufacture of precision castings, it was decided that the Mercast process offered the best method for the production of the high quality castings required by the aircraft, electronics and gas turbine industries. Sankey-Telcon is the sole operating licensee of the Mercast process outside the U.S.A., and after a preliminary development period has been operating on a production basis for about eighteen months at the new works at Manor Royal, Crawley.

The Mercast Process

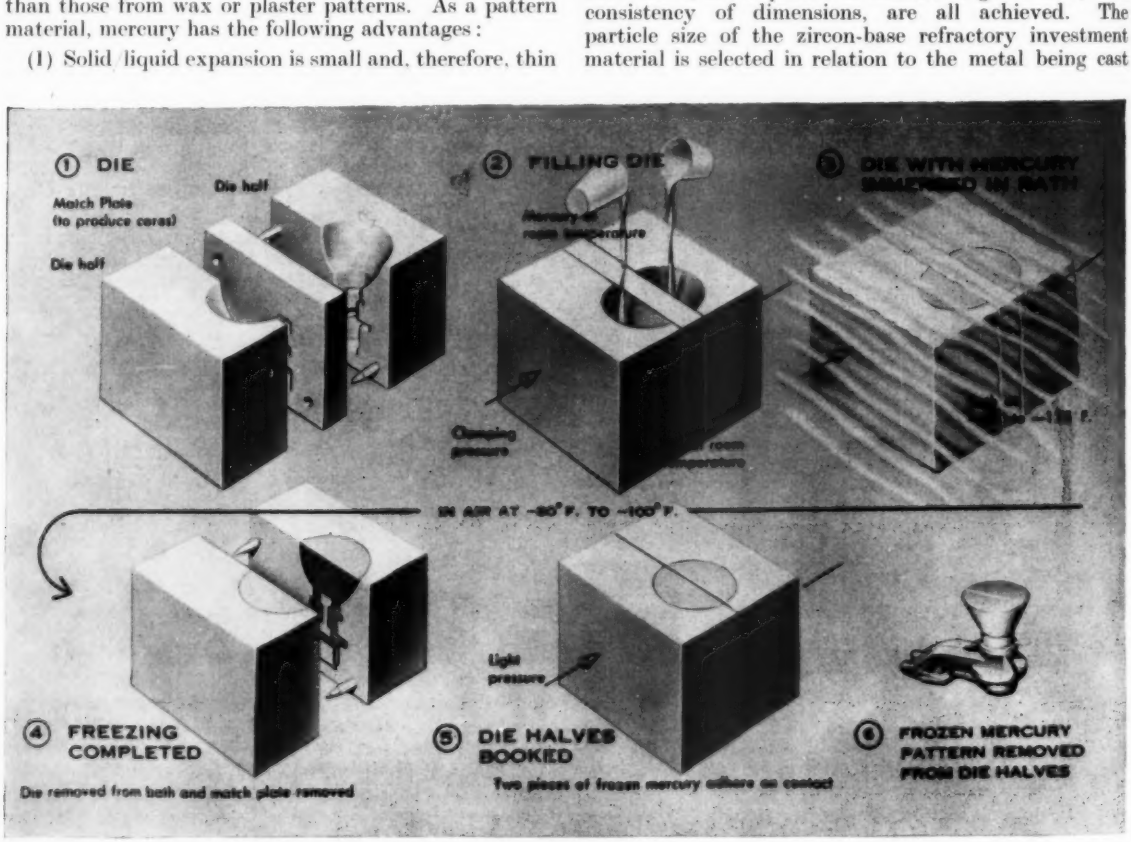
In the Mercast process, frozen mercury is used as the pattern material, and it is claimed that it enables castings to be produced of better quality and greater intricacy than those from wax or plaster patterns. As a pattern material, mercury has the following advantages:

(1) Solid liquid expansion is small and, therefore, thin shell moulds can be employed without fear of cracking the shell.

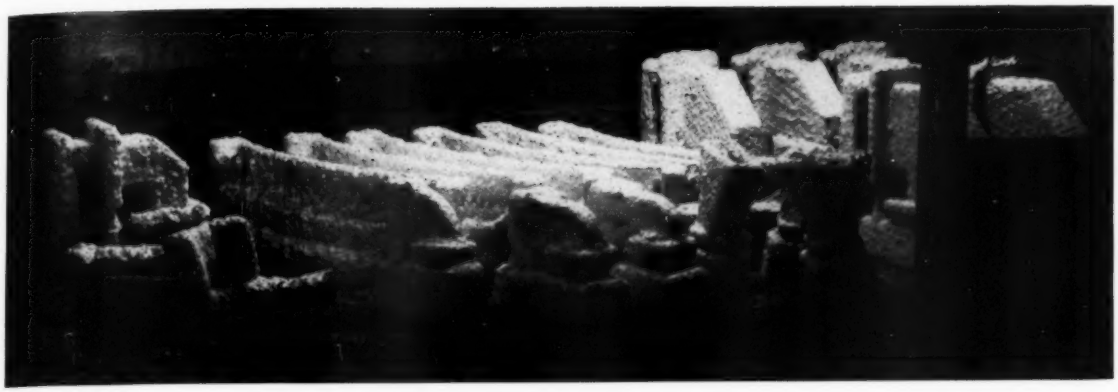
(2) It readily welds to itself under light pressure, so that accurate and intricate patterns can be produced by abutting or "booking" simple component patterns together in a precision jig. This characteristic also enables cores to be positioned in sites inaccessible in other techniques.

(3) Its high density and good wetting characteristics permit perfect reproduction of minute detail.

The zircon-base refractory material, free from all moisture, combined or absorbed, together with the mercury pattern enables a shell mould to be produced, which, after firing, is strong, stable and inert to most alloys. The shell mould, as compared with the block mould produced by other investment techniques, permits preferred metallurgical practice to be employed during casting. Freedom from porosity, shrinkage cavities and blow holes, development of controlled grain size, and consistency of dimensions, are all achieved. The particle size of the zircon-base refractory investment material is selected in relation to the metal being cast



Diagrammatic representation of the Mercast process.



A selection of Mercast shell moulds.

and enables a fine surface finish to be attained on the casting.

The shell moulds enable chills to be used, allowing directional solidification to be induced, even in those cases where rapid changes in cross-section occur. The strength of the thin shell mould is sufficient to withstand the most severe mechanical shock associated with casting by suction, vibration, inversion, centrifugal or vacuum methods.

Mercast castings serve engineers in many industries, and it is claimed that specific design requirements unattainable by other techniques can now be met. Furthermore, more accurate castings with better surface finish, more complex castings, and castings with exceedingly good mechanical properties can be readily produced.

A general guide to tolerances obtainable is + 0·003 in. /in. for most alloys, but somewhat closer tolerances are attainable for aluminium alloys. This tolerance does not increase proportionately with length, e.g. castings with a linear length of 9 in. can be held to a tolerance of + 0·018 in. Concentricity and flatness is another superior characteristic of Mercastings, and these particular factors are all-important in the application of the process to the fuel valves used in missile power units. With regard to surface finish, aluminium alloys have a cast finish of 30–40 micro inches r.m.s., copper alloys 50–60 micro inches r.m.s., ferrous alloys of low alloy content 100–150 micro inches r.m.s., and of high alloy content 50–100 micro inches r.m.s.

Mechanical properties attained by the Mercast process are claimed to be better than those normally obtained by other casting techniques. Indeed in the U.S.A. castings are in current production with an ultimate tensile strength in excess of that obtainable from forged components.

New Works

Plant was installed at Crawley in 1955 to permit experimental production. By mid 1956, this preliminary exploration of the technique was complete and the new factory, with an area of 5,000 sq. ft. of factory space and 1,000 sq. ft. for radiographic examination, drawing office and general offices, was planned. A.I.D. chemical analysis and associated facilities are made available by The Telegraph Construction & Maintenance Company, on whose site, the new factory is built.

The factory is divided into three main units; viz. pattern and mould making, foundry and finishing, and tool making. It has ample natural lighting and ventilation; in certain hazardous locations the natural ventilation is assisted by forced ventilation. This applies particularly to the pattern and mould making shop and sections of the foundry. Heating is by low pressure steam.

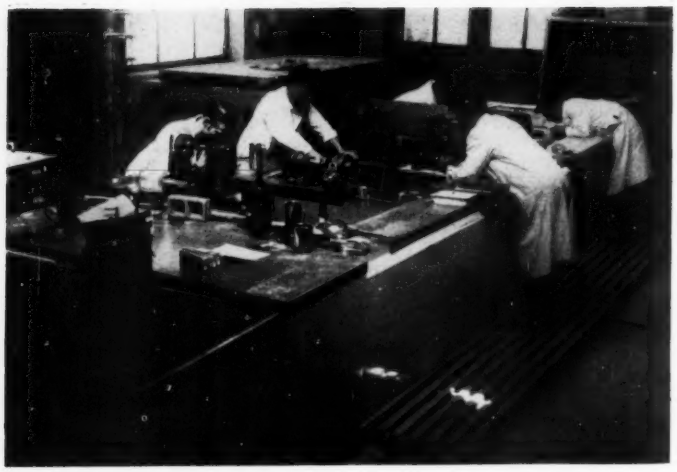
Pattern and Mould Making Shop

The essential plant in the pattern and mould making shop consists of two insulated tanks, having internal dimensions 11 ft. × 4 ft. 6 in. × 4 ft. 9 in. deep and 6 ft. × 4 ft. 6 in. × 4 ft. deep, the former being known as the freeze tank and the latter as the dip tank. These tanks are maintained at a temperature of—63° C to —67° C. and—60° C. to—63° C., respectively, by means of a mechanical refrigeration unit housed in a totally enclosed room. Mercury in the dies is frozen in the freeze tank and these frozen mercury patterns, after extraction from the dies, are invested with the zircon-base ceramic in the dip tank. To speed up the freezing, the freeze tank is filled with acetone to provide an adequate thermal sink. Because of the consequent fire hazard, all lighting and electrical equipment in this shop is flameproof, and in so far as it has been possible, compressed air is used for operation of hoists, slurry stirrers, etc., although flameproof electric motors are used for slurry mixing. It is because of the fire hazard that the mechanical refrigeration is in a totally enclosed room, outside the pattern and mould making shop, on the far side of an explosion wall.

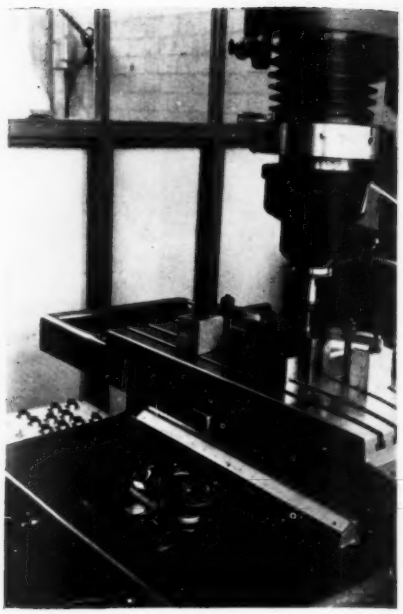
Ancillary equipment includes:

A Melt-out Rack.—It is here that the invested frozen mercury patterns are allowed to warm up when the mercury melts and runs out of the moulds. Directional melting may be induced by projecting a stream of liquid mercury at room temperature on to specific sites on the pattern. The mercury runs into a trough underneath the melt-out rack, where it is covered by a layer of acetone which suppresses the formation of mercury vapour. The mercury is returned from this unit through a cleaning system back to the freeze tank, for the making up of further patterns.

Warm-up Tanks.—These tanks are filled with acetone and are maintained at room temperature by a steam heating coil. As the tools are dissembled after the free-



A view of the pattern and mould making shop.



The 3 S.M. Hauser jig grinder.

zing operation, they are returned to this tank, where their temperature is brought up to room temperature prior to reassembly and following through the next cycle.

Slurry Mixing Unit.—This unit is used intermittently for the making up of the investment slurries. It consists essentially of an insulated tank fitted with two stirrers operated by flameproof motors. Because of the intermittent nature of its use, this tank is cooled with solid carbon dioxide rather than by the mechanical refrigeration unit, which operation would unnecessarily increase its peak load and consequently its size.

An elaborate ventilating system is installed to remove acetone vapour and mercury vapour. The latter might become a health hazard, and adequate precautions are taken to ensure that the concentration never reaches a level at which danger to the health of operatives might occur. An automatic carbon dioxide vapour system is installed over the freeze tank, and there are fusible links on the lids of the warm up tanks which would be brought into operation should fire occur.

Foundry and Finishing

Apart from melting furnaces, the foundry is equipped with furnaces for firing moulds and for preheating mounted moulds for the casting operation. High alloy steel is melted in 20 lb. capacity rocking hearth indirect arc furnaces, or in 20 lb. capacity high frequency spark gap furnaces. Aluminium alloys are melted in a 70 lb. capacity electric resistance furnace of the bale-out type, and a 100 lb. capacity gas-fired tilting furnace is used for the melting of copper-base alloys.

The green moulds from the pattern and mould making shop are first dried in an infra-red cabinet, and are then fired at high temperatures in a trolley hearth electric furnace. This furnace is designed with heating elements in the floor, roof and walls, so that the temperature distribution in it is practically uniform. In case there may be traces of mercury left in the green moulds, both the infra-red heated drying cabinets and the firing furnace are fitted with forced draught ventilation. The fired moulds are mounted in various ways and preheated to the required temperature for casting in trolley hearth electric furnaces. Depending upon the complexity of the mould and the alloy being cast, inversion pouring or simple open pouring may be employed, but more usually sling, vibration, centrifugal or suction casting is used. The moulds being strong and porous, are readily adapted to any of these processes. Apart from these more conventional methods, the moulds are ideally suited to casting *in vacuo*, and a 56 lb. capacity vacuum furnace is employed for this purpose. As the moulds are porous and free from any moisture, entrapped gases and air are completely avoided, and thin shell moulds are readily heated on the inner face without involving substantial temperature gradients from the outside to the inner face of the cavity. A further invaluable feature is that these moulds require less space than the block type, and many more can be mounted inside the restricted space available in the chamber of the vacuum furnace.

The finishing section is equipped with a high speed handsaw, abrasive cut-off machine, shot and vapour blast cabinets, grinders, linishers and the usual bench finishing tools.

The inspection department covers both A.I.D. and A.R.B. requirements, and has all the necessary facilities for radiographic examination, crack detection, dimensional inspection, etc. All castings are approved by this department prior to despatch.

Tool Making

To produce castings to close dimensional tolerances, the patterns taken from the dies must be to even closer dimensional tolerances. This alone requires a high standard of tool making. To this must be added the fact that to, avoid leakage of mercury, adjacent faces must mate with a clearance not greater than 0·0005 in. and it is evident, therefore, that the dies must be of the closest dimensional accuracy. The toolroom equipment includes lathes, millers and grinders of such a calibre as to enable

this high precision to be attained. Of particular interest are :—

The 3 S.M. Hauser Jig Grinder.—This grinder is capable of jig grinding holes and slots to + 0·0001 in. and covers the size range from 1/32—3 in. diameter, inclusive. This facility is essential in obtaining accurate alignment of the various parts of the dies.

The 8–18 Cincinnati Tool and Die Mill.—Various shapes including aerofoil sections and complex cavities are produced on this machine.

Typical Castings

Components for Aircraft and Industrial Gas Turbines

A typical casting currently being produced is an outer flange segment which is welded to the exit of a combustion chamber in a jet engine. Guide vanes formed from sheet metal are welded in each of the aerofoil slots, a lip being cast on to allow successful welding to be carried out.

The part is cast in Nimocast 90, a heat resisting alloy containing titanium and aluminium. Partly because of the nature of the alloy, the casting is difficult to produce to the required tolerances. The aerofoil shaped slots are held within a zone of 0·003 in. on the envelope, and the positional accuracy within 0·010 in. of the centre slot. The radius of curvature is held within ± 0·010 in. The finish machining is reduced to a minimum, as this is essential when a difficult machining alloy such as Nimocast 90 is used.

Every casting is subjected to X-ray examination and crack detection, and close control on analysis is maintained. The casting is finally delivered in the solution heat treated condition.

Another type of casting produced is a multi-bladed rotor cast in an austenitic heat resisting steel. Close control on dimensions is essential, especially in respect of concentricity, or difficulty in balancing results. On such a rotor, concentricity is held within 0·015 in. T.I.R. on a diameter of 6 in.

Other castings produced include stator blading for industrial and aircraft gas turbines. The standards of acceptance are very high in both cases, and dimensional accuracy must be maintained consistently. Such castings are now being produced by vacuum melting and casting, this being especially useful for high temperature alloys containing easily oxidisable constituents such as titanium and aluminium.

Missile Components

Some castings have been produced for this field of engineering, mainly for the control systems. An LM.15 aluminium alloy gyro gimbal of rectangular shape with internal bracing members and with mounting holes has been produced. This was cast close to finished size, leaving a minimum of machining. Such a cast part has proved to be inherently more stable than equivalent forged and machined components.

A Centimetric mixer unit, cast in aluminium alloy LM.8, with complex coring is being manufactured in two halves, the various channels being held to an accuracy of ±0·004 in. or ±0·002 in. Tolerances on positional dimensions of channels in relation to one another are from ±0·004 in. to ±0·002 in. The only machining carried out on these castings is on the abutting faces, and in drilling holes to enable them to be fixed together. The maximum misalignment of the two halves is held to within the above tolerances. The surface finish is approximately 30–35 micro inches r.m.s.

Parts for Radar and Electronic Equipment

Many types of waveguides including tight bends, horns, etc., for such equipment are being regularly manufactured. Both E and H plane bends with integrally cast flanges are produced in S and X bands. These are cast in aluminium alloy LM.8, which is the best available compromise between machinability and castability, or in gunmetal. Tolerances consistently maintained are ± 0·002 in. on the 0·9 in. and 0·4 in. dimensions, and ± 0·004 in. on the 1 in. and 3 in. dimensions. Surface finish is maintained at 25–35 micro inches r.m.s.

As flanges are cast on, the only finishing necessary is the machining of the flange faces, including choke grooves, and the drilling of fixing holes. Complex horns containing transfer sections have proved to be particularly suitable for the process, as they are very difficult to produce by fabrication techniques in aluminium alloys.

Potentialities

Small Turbine Wheels, Inducers, Exducers, etc.

If the gas turbine is to be used successfully in the automotive field, the necessity for a manufacturing technique capable of producing satisfactory turbine wheels in difficult machining alloys economically is obvious. It is considered that the only feasible technique is by casting, probably vacuum melting and casting, particularly if the alloys required contain easily oxidisable constituents such as aluminium and titanium. Because of the advantages of the Mercast process, it is believed to be best adapted of all the casting techniques to meet the stringent requirements of this type of casting. Similar considerations apply to the manufacture of turbo-charger components for diesel engines. Initial tool costs may be high, but these are readily offset in quantity production.

Blading for Land and Marine Gas Turbines

As design requirements for these turbines call for

A section of the inspection department.

higher operational temperatures and great reliability, many relatively new materials, such as the so-called super alloys, must be used to meet the creep, fatigue and thermal shock requirements. Some of these alloys are very difficult, if not impossible, to forge and machine and, as a result, the designer may have to limit himself to relatively simple forms and alloys with inadequate properties. Alternatively, he can use precision castings with the consequent greater freedom in design and choice of materials.

Experimental work on the production of blades for gas turbines has shown that complex blades can be cast by the Mercast process with a sound metallurgical structure. The blade angles, the forms of appendages, relatively sharp changes of cross-sectional areas, the inclusion of cavities to meet temperature distribution requirements, etc., can all be met, and no problems arise as to whether the design can be machined, forged or fabricated. General dimensional tolerances are ± 0·005 in. but in fact the dimensions are usually held from ± 0·003 in. to ± 0·005 in. Surface finish of 40–65 micro inches r.m.s. is attained, depending on the alloys used, and this, coupled with the design features, minimises turbulent flow and improves efficiency.

Rotor Blades for Aircraft Gas Turbines

As the operating temperature of gas turbines is increased, it becomes more and more difficult to manufacture them by conventional forging and machining methods. It is considered that eventually, despite current prejudice, cast rotor blades will be used in British gas turbines. It is envisaged that the blades will be produced by vacuum melting and casting in highly complex alloys, probably designed as casting alloys and incapable of being hot worked or machined.

Structural Castings for Aircraft and Missile Airframes

The use of high strength castings in this field is already widely developed in the U.S.A. A suitable casting technique gives the following advantages :

(*i*) High strength, e.g. 115 tons/sq. in. U.T.S. with 10% elongation.

(*ii*) High strength to weight ratio, although here design plays a very large part in gaining the maximum advantage.

(*iii*) Space saving, which is of vital importance as extensive equipment has to be installed in modern airframes, so that only limited space is available for structural components, which are also consequently usually of awkward shape. Forging and machining of such components is often difficult.

The Mercast process is claimed to be particularly suited to the manufacture of such components for the following reasons :

(1) Thin walls can be successfully cast.

(2) Large and heavy shapes can be made.

(3) Complex shapes can be produced.

(4) A high degree of metallurgical control is possible.

At the present time precision castings are relatively new to designers and engineers and, as such, are suspected by many and accepted by few. It is, however, certain that these will be extended to wider and wider fields and, at least in some, eventually completely replace parts produced by other methods.

Vitreous-Enamelled House Chimneys

A COMPLETE range of vitreous-enamelled chimneys—claimed by the manufacturer to be the answer to condensation attack—is now being developed by Ferro Enamels, Ltd., of Wolverhampton. The chimneys are of the self-supporting type—from ground floor to roof level—and are made from enamelled steel, which is further protected by high-temperature building insulation wrapped around the steel liner ; expansion joints are provided for variable temperature conditions. The chimney stack can be matt-finished in any colour, or in a special enamel brick finish, and have welded flashing incorporated in the construction to facilitate easy installation to any roof angle. The company is also developing sectionalised chimney linings for use in existing brick-built chimneys.

Library Guide

"WHAT'S AVAILABLE IN THE TECHNICAL LIBRARY," by the librarian of the Manchester Technical Library, offers students, research workers and "do-it-yourself" laymen an admirably informative survey of the library's resources other than its 80,000 books. Over 1,600 scientific and technical periodicals are currently received and, to enable readers to make full use of the files, Mr. Taylor describes the many periodical indexes, abstracting services and other bibliographical aids available. The library's collection of patents, standard specifications and atomic energy documents are also described. A well-chosen list of guides and bibliographies ends the pamphlet. Copies can be obtained, free of charge, from the Technical Librarian, Central Library, Manchester, 2. (TELEX 66–149 or Tel. : CEN. 7401).

New Company

CONTINENTAL CAN COMPANY, INC., of New York, and Vacuum Research (Cambridge), Ltd., have formed a company, Vacuum Metallizing Processes, Ltd., registered in the United Kingdom, for the purpose of promoting and licensing in all territories outside North and South America their jointly developed and patented process for the metallizing in vacuum of plastic films and paper on a commercial basis. Vacuum Research (Cambridge), Ltd., has been responsible for the design, construction and installation of production metallizing facilities now operated by Continental Can Co., Inc., and their licencees in the U.S.A. The two companies are continuing their development work on this process, and its commercial applications. The process is suitable for a wide variety of applications including the packaging, electrical, textile, paper and plastics industries.

Fielden Midland Office

FIELDEN ELECTRONICS, LTD., have established a permanent Midland Area Office at 51 Bradford Street, Walsall, Staffs. (Tel. : Arboretum 55343), under the management of Mr. F. B. Price.

Some Impressions of the Continental Steel Industry

By G. R. Bashforth, F.I.M.

SOME ten years had passed since the manuscript of Volume II—"Steel Production" of the author's book, "The Manufacture of Iron & Steel," had been completed. The possibility of a revision had been envisaged and several hundred papers, abstracts and notes had been filed, covering new work and developments. They had been indexed to facilitate their inclusion in any revised edition. When the final arrangements were being made for this revision, it was appreciated that the inclusion of such a quantity of new material would make the volume too massive, and it was decided to divide the work into two parts. Volume II, which is now going to press, deals with steelmaking in general, whilst Volume III covers fuels, furnaces, refractories and instruments used in the manufacture of steel. The third volume is nearing completion, but the author felt it desirable to verify personally some of the data which had been collected over the years before actually including it in the new work.

Several of the papers and abstracts collected referred to developments in the design and operation of open hearth furnaces in Germany. Modifications had taken place in the operation of Bessemer converters and two new processes—the L-D and the Rotor processes—had been evolved. There were also numerous claims from the Continent regarding the development of continuous casting, and these developments were felt to be of sufficient merit to warrant further investigation. It was decided, therefore, to visit the Continent, but in view of the time available works visits had to be curtailed and greater importance placed on discussions with persons in authority. When necessary, such as the verification or clarification of some point, these discussions were followed by visits to particular parts of the plant.

Fuel Policy

There appears to be a fairly well defined fuel policy. Most of the German open hearth furnaces are operating on cold coke oven gas illuminated with either oil or lignite. This coke oven gas, usually referred to as Ruhrgas, is supplied from a grid system, and although plentiful in summer months, there may be some shortage during the winter, which necessitates the availability of an alternative fuel. The alternative fuel is generally fuel oil. The author was informed that some years ago several furnaces were changed to oil firing, but owing to excessive wear on refractories there had been a general reversion to carburetted coke oven gas. German coal tar oil is more expensive than imported mineral oil, but the sulphur content is much lower. It is the general policy, therefore, merely to employ liquid fuels as an alternative fuel or as an illuminant.

Some supplies of natural gas are available, but it would appear that the quantities are comparatively small. Natural gas is used, however, at the Klockner works in Osnabruck and Georgsmarienhutte. At some of the composite works, a two or three gas mixture is used in the open hearth plants. Where this policy is employed the coke oven and blast furnace gases are mixed so as to give a calorific value of about 2,000 k.cal./cu. m., which is approximately 225 B.Th.U./cu. ft.

Experimental work of special interest is the oxygen enrichment of the blast in producer gas practice. By increasing the oxygen content of the blast to 25–27%, it is possible to increase the calorific value of the gas from 1,450–1,500 k.cal./cu. m. to 2,000 k.cal./cu. m., which is approximately 225 B.Th.U./cu. ft. Obviously, this practice substantially reduces the nitrogen content of the gas, and since a higher proportion of steam is necessary to control the heat within the producer, there is an increase in the hydrogen content of the gas. It is doubtful whether this practice would justify the installation of a bulk oxygen plant, but where such a plant is already available, developments along these lines would appear to merit serious consideration.

Furnace Design and Availability

Since the author's previous visit to Germany in 1953, there have been some changes in furnace design, and it would appear that in the new open hearth steelworks the general arrangements and layout should permit more rapid furnace repairs as a result of greater mechanisation, thereby giving a higher furnace availability. In these new plants, the increased nominal capacity of the furnaces is perhaps a noticeable feature. At both Klockner-Hutte A.G. and at August Thyssen-Hutte, Homborn, there are four open hearth furnaces built to the Loftus design. At the former the furnaces are of 225 tons capacity and at the latter 250 tons capacity.

At the Mannesmann, Huckingen plant, there are four Maerz type furnaces of 150 tons capacity, whilst two 120 ton furnaces of Demag design have been erected at Westfalenhutte, Dortmund. It would appear that preference is still given to fixed furnaces, although tilting furnaces of Demag design have been erected at Phoenix-Rheinrohr Werk, Mulheim, and Klockner A.G., Georgsmarienhutte. At the Phoenix plant the furnaces have a nominal capacity of 150 tons, whilst at Klockner they are 200 ton furnaces.

The variation in furnace design can be appreciated, but Maerz type furnaces still attract considerable interest. In most cases these furnaces have been changed from twin-uptake to single uptake design, which would appear to be in keeping with the results obtained in the investigations carried out both in this country and abroad. The Maerz design does possess several advantages, such as economy of space, economy of brickwork and hence labour saving, and gives excellent flame conditions, which permit rapid rates of driving.

All the Maerz furnaces seen by the author were fired with either oil or carburetted coke oven gas. On

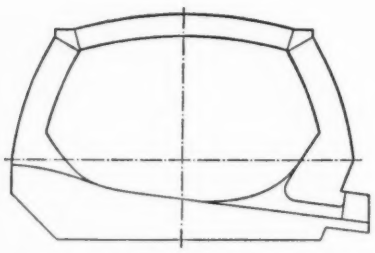


Fig. 1.—Lines of the Maerz-Boelens O.H. furnace.

the coke oven gas furnaces multi-burners were employed. It is customary to use the outer two burners during charging and melting down, reverting to the use of a single central burner during refining, when a lower heat input is desired. Although this type of furnace appears to give a very hot flame, which facilitates very rapid melting, flame direction would seem to depend on the velocity of the incoming fuel. In the case of one furnace fired with producer gas, the gas pressure in the uptake was 40 mm., which few plants in this country could satisfactorily maintain. The author feels, therefore, that although this design may be very satisfactory where oil fuel or carburetted coke oven gas is available, it is not to be generally recommended for producer gas firing, unless very high gas pressures can be maintained. It also appeared that the atmospheric oxidation in this design of furnace was higher than in the conventional designs, which, of course, would be an advantage when manufacturing low carbon steels.

An interesting modification of the Maerz furnace is the Maerz-Boelens design, which was developed by F. Bartu of Zurich and E. Boelens of Liege. The chief characteristic of this modification, which is shown in Fig. 1, is the inward batter of both back and front walls. In the more conventional types of furnace with a sloping back wall, which permits the fettling to be carried up to the roof, the roof span may become somewhat excessive, with consequent weakening of the roof structure. With the inward slope in the Boelens design, the roof span is reduced, but more refractory, which is not so easily replaced, is exposed to the flame. Although some reduction in refractory consumption has been claimed as a result of the adoption of this design, there would appear to be other even more important benefits to be derived.

It has been suggested that the new design promotes better heat transfer between the flame and the solid stock. It is claimed that the narrower laboratory prevents the spreading of the flame after it has struck the solid stock in the furnace, since it remains more concentrated in the confined area between the stock and the roof. Some figures appear to indicate that this design may give a 15% fuel economy with about 8–10% increase in productivity.

Several furnaces of this design have now been erected in Germany, Sweden and France, and very encouraging reports have been circulated. These reports appear to indicate that a lower overall refractory consumption can be anticipated, although there is an increase in the fettling along the slag line immediately below the inward sloping front and back walls. There is some fuel economy linked with increased productivity. Perhaps, however, it is too early to be dogmatic about the advantages of this design.

There are several plants in Germany, like some of the older plants in this country, which are very congested. This lack of space does not permit a high degree of mechanisation to effect rapid furnace repairs. A high furnace availability can only be achieved, therefore, by either simplification of furnace design or by improved furnace life, or both. It is perhaps for this reason that the Maerz furnace commands such interest. It is economical in space and the volume of brickwork is reduced to a minimum. One method of improving furnace life is the adoption of the box-type roof.

The Kreutzer Box-Type Roof

Undoubtedly the box-type roof developed by Dr. Kreutzer has given an increase of 40–50% in roof life compared with the life of ordinary ribbed roofs. This type of roof may be constructed with either silica or basic refractories, but the greatest advantages appear to accrue from silica roofs. Although many basic roofs are in operation, it is by no means an accepted practice. German experience seems to be similar to English and American experiments, which have demonstrated the susceptibility of basic roofs to thermal shock and increased complications in roof construction. Although satisfactory in hot metal processes, where a reasonably constant heat may be maintained, the basic roof will not accommodate such frequent and sudden changes in temperature as are encountered in cold metal practice.

The box-type roof, shown in Fig. 2, is a development of the ribbed roof, but the ribs running transversely across the furnace are reinforced by longitudinal ribs extending the whole length of the furnace. These ribs, which are about 50% thicker than the rest of the roof, form a box-like structure affording great rigidity. In the more vulnerable portions of the roof, such as along the backwall and in some cases over the charging doors, the longitudinal ribs are closer together, thereby forming smaller boxes. This system of construction gives increased rigidity during the early part of the furnace campaign, and permits more durable repairs to be effected when the roof has worn thin.

When a particular piece of the roof has burnt to a thickness of about 25 mm., slightly less than one inch, any dust is removed from the surface of the roof and a dry jointing material is placed over the hot spot and the filler bricks inserted between the ribs, as shown in Fig. 2. When the boxes have been filled, a further quantity of this jointing material is spread over the filler bricks, thereby sealing the spaces between the new brickwork. This jointing material appears to be a fairly low melting point refractory which possesses the property of converting the portions of the original roof and the filler bricks applied into a monolithic mass. In many of the samples examined by the author, it was impossible to detect the line of demarcation between the original and new brickwork.

One interesting feature of most of these box-type roofs was the method of air cooling shown in Fig. 3. Jets of compressed air were blown over the outer surface of the roof. Although this air cooling was not considered essential, it was regarded as a definite advantage. In addition to its cooling effect, it does keep the roof surface free from dust and dirt, which acting as an insulator increases the roof temperature, and it also ensures that there is no barrier between the original roof structure and the jointing compound on which the filler bricks are applied.

Several records of this type of roof were examined

which indicated that an increased roof life of 50% or more could be anticipated. This type of roof has, of course, been tried in this country and somewhat indifferent results have been obtained. In some cases it would appear that the failure to obtain the benefits claimed was due to the application of the filler bricks too soon, that is before the original roof had burnt back to the requisite thickness. The actual thickness of the roof before the application of the filler bricks is an important feature. The roof should be showing a good red heat and the filler bricks should be inserted whilst the original brickwork is at a sufficiently high temperature to allow the monolisation of the old and new work.

The author feels that the results obtained in Germany with this type of roof merit further investigation in this country. It is possible that its adoption here would achieve considerable improvement in roof life and hence furnace availability.

Furnace Instrumentation

There appears to be ample evidence that the Germans are becoming even more convinced of the importance of instrumental control of furnace operation. It is encouraging to learn that instruments of British manufacture are finding an increasingly ready market. Perhaps this fact is not surprising in view of the rapid strides which British instrument makers have accomplished in recent years. In this country the application of instruments to furnace control coincided largely with adoption of oil-firing, but events have demonstrated the greater efficiency which can be achieved by the employment of instruments on any furnace, irrespective of the mode of firing.

The Use of Oxygen

The use of gaseous oxygen has probably been more extensively developed on the Continent than in this country. Its earliest application appears to have been in connection with the Bessemer process, in an attempt to reduce the nitrogen content of the steel produced, thereby rendering it more suitable for special purposes, such as deep drawing. Its employment was increasing, however, at the time of the author's previous visit in 1953. Even at that time several plants were experimenting with the desiliconisation of blast furnace metal in the transfer ladles by means of an oxygen lance.

Ladle desiliconisation of blast furnace metal is now extensively practised on the continent, even as it is in this country. Usually the metal is treated in batches of 20–30 tons in ladles having a capacity of 30–40 tons. This precaution of having the ladle only two-thirds full is to counteract the effect of ladle reactions which may cause serious slopping.

Prior to oxygen lancing, about 2% of lime, depending

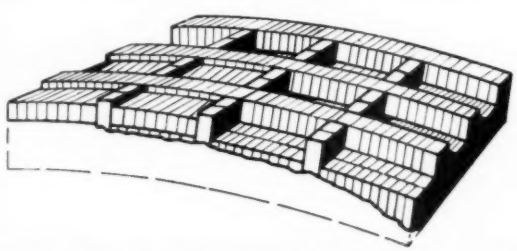


Fig. 2.—Kreutzer box-type roof after insertion of the filler bricks.

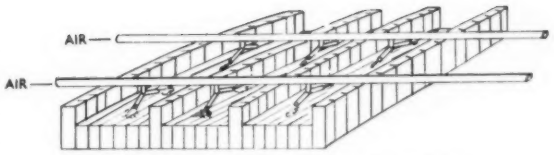


Fig. 3.—Ribbed roof showing air cooling.

on the silicon content of the metal, is added to the ladle to form a receptive slag. A hood is placed over the ladle so as to convey any fumes arising into a suitable stack, and the oxygen lance is inserted through a hole in this hood. The oxygen consumption is at the rate of about 60 cu. ft. per 0·1% of silicon removed per ton of metal treated. In order to reduce the trouble due to foaming or slopping, the rate of lancing is normally restricted to 200–250 lb/sq. in. In this manner the silicon content of 20 tons of metal can be reduced from 1·0% to 0·4% in about half an hour, with an oxygen consumption of some 7,200 cu. ft.

This method of pretreatment is very beneficial, as it allows the blast furnace plant to concentrate on the production of a low sulphur pig iron, with the knowledge that if this low sulphur is accompanied by a high silicon, the silicon can be reduced in this manner. Since the reactions are exothermic, the metal gains heat during treatment, which is another advantage.

One natural development of the use of oxygen in the Bessemer process and the desiliconisation in the ladle, appears to be the "top-blown" converter practice, or L-D process, which has been so successfully introduced at Linz and Donawitz in Austria. This process has been fully described in several excellent articles in the technical press, but perhaps the most informative account is that published by Voest[1]. It must, however, be agreed that this publication is issued by the inventors and developers of the process, and may therefore be a little prejudiced.

The author has had the opportunity of investigating this process through the media of first hand investigators, and has had practical experience of the properties and suitability of the steel produced for various applications. The process does offer a very economic method of steel production, with a high rate of productivity linked with low capital expenditure. The quality of the steel produced is at least equivalent to that of bulk ingot production by the basic open hearth process.

In the top-blown oxygen converter process, the conversion is performed in a solid bottom pear-shaped vessel into the throat of which an oxygen lance is lowered to a distance of 25–40 in. above the surface of the metal. In a 30-ton capacity converter this water-cooled oxygen lance or pipe would be $1\frac{1}{4}$ in. diameter and the oxygen injected at a pressure of about 250 lb./sq. in., which means the oxygen rate would be about 2,000–3,000 cu. ft. per min.

Lime or limestone, amounting to between 4 and 6% of the metal charged, is added by means of an overhead chute. In order to ensure satisfactory contact between the oxygen and the metallic bath during the early stages of the process, which might be hindered by solid lime floating on the surface of the bath, about one-third of the requisite lime is kept in reserve and is added by means of an overhead chute, without interruption to the process, after blowing has been in operation for some five to ten minutes. Immediately the oxygen injection is com-

menced, a slag is formed by the lime and the iron oxide resulting from interaction between oxygen and the iron. As blowing proceeds the slag/metal reactions continue, bath temperature and slag composition being controlled by steel scrap and/or lime additions.

The end point is indicated by the disappearance of the carbon flame, since there is no after-blow due to the fact that phosphorus can be eliminated throughout the blow, providing that slag composition and temperature are correctly controlled and the pressure of oxygen impingement is regulated. The relative rates of carbon and phosphorus removal appear to depend on the pressure at which the oxygen is injected. High pressure oxygen results in a spray of metal which, becoming oxidised, accelerates carbon removal. A low pressure impingement of oxygen above the surface of the bath favours greater slag/oxygen contact, with a resultant acceleration of phosphorus elimination.

There would appear to be some difficulty in the precise regulation of these conditions, which perhaps accounts for the fact that this process is generally limited to the conversion of low phosphorus pig iron of the stahleisen type. In other words, it is a process for the conversion of those types of pig iron normally employed in the basic open hearth process on the continent. For such irons, it offers a very economic method of conversion, involving comparatively low capital costs and affording a high rate of productivity. This process is ensured further adoption in those districts where suitable iron is available, or can be produced. The latest development appears to be the new oxy-steel plant at the Royal Netherlands Blast Furnaces & Steelworks at Ijmuiden. This plant will have an annual capacity of 300,000 tons, suitable pig iron being smelted in their own blast furnaces.

In the rotary oxygen processes developed in Sweden, and at Oberhausen, in Germany, the control of the respective rates of decarburisation and dephosphorisation appears to be simplified to some extent by the rotation of the bath during conversion, and by the angle and pressure of oxygen impingement. In both these processes, the fundamental difference as compared with top-blown converter practice would appear to be the rotation of the hearth during oxygen injection. This rotation ensures better slag metal contact. This feature permits the employment of higher phosphorus pig irons, which can be successfully refined with the production of a high grade steel.

The rotary steelmaking process developed at Oberhausen is operated in a rotary furnace some 48 ft. long with an internal diameter of 8 ft. 10 in., having a capacity of 60 tons. At one end of the furnace there is an opening for the charging of pig iron and slag making materials, and for the introduction of the oxygen lances. At the opposite end there is another opening for the escape of exhaust gases. This furnace is lined with magnesite bricks faced with rammed tarred dolomite. The speed of rotation can be varied between 0·1 and 0·5 r.p.m.

The oxygen is admitted through two circuits, which are independently controlled, thereby permitting the volume, pressure or concentration in either circuit to be varied as required. The primary oxygen, which performs the oxidation and stirring of the bath, is introduced through a water-cooled lance or nozzle under the surface of the bath. The secondary oxygen is admitted above the surface of the bath for the combustion of the carbon monoxide resulting from the refining operations. The metal is tapped through a taphole sited at the exhaust end of the furnace. Tilting mechanism is provided to facilitate the removal of slag.

When operating with high phosphorus pig iron, a double slag process can be employed. After the charge has been blown down to about 2·0% carbon and not more that 0·1–0·2% phosphorus, the low-iron high-phosphorus slag is tapped off for use as a fertiliser. A second slag for final dephosphorisation is then made by further additions of lime and iron ore.

The quality of the steel produced by this process is very satisfactory, being equal to the ordinary grades of steel produced by the basic open hearth process. Providing the state of oxidation is carefully controlled, whereby the cleanliness of the finished steel is largely governed, there is no reason why steel produced by either rotary steelmaking process or by top-blown converter practice should not replace basic open hearth steels in many higher duty applications, such as deep drawing and the manufacture of even seamless tubes by a rotary piercing process. The author is convinced that some of the failures attributed to the oxygen steel processes have been due rather to faulty casting pit practice than to the nature of the actual process of steelmaking.

Continuous Casting

There appears to be some evidence to indicate that the development of continuous casting has been more rapid on the continent than in other parts of the world. The obvious economic advantages of continuous casting, such as the elimination of ingot moulds and carriages, soaking pits, cogging mills and all their ancillary equipment, will be a great impetus to its further development and perfection.

Since continuous casting has been developed along several independent lines and for the production of varying qualities of steel, one must anticipate differences in the design of the plant and equipment employed at the several works. The general principle and essential features of all continuous casting machines are similar. The metal is tapped from a conventional steelmaking furnace into a preheated ladle, from which it is poured through a tundish into a water-cooled mould. At the commencement of casting the bottom of this mould is sealed with a dummy billet on to which the steel solidifies. As soon as the liquid metal reaches the desired level in the mould, withdrawal of the dummy billet begins, and as casting proceeds the desired height of liquid in the mould is maintained by regulation of the speed of pouring and the rate of withdrawal.

When the billet leaves the bottom of the mould it passes through a secondary cooling chamber, which is equipped with a series of water sprays, whereby the complete solidification of the steel is facilitated. Below this chamber there are the withdrawal rolls and a moving oxygen flame cutter, by which the billets are cut into the requisite lengths before their discharge into a suitable transfer device.

The method adopted for pouring the steel from the ladle into the mould appears to depend on the size of the installation. When handling small charges of steel at a comparatively slow rate of a few tons per hour, lip pouring is favoured. The temperature variation when lip pouring from a 5 ton "tea-pot" type ladle may be 90-100° C., being of the order of 1,600° C. at the commencement and falling to 1,500°–1,510° C. at the end of teeming. Under these conditions the rate of casting

can be more easily controlled with lip pouring. For dealing with larger quantities of metal, bottom pouring through a nozzle in the base of the ladle is advocated. The temperature variation when teeming a heat through a nozzle from a 20 ton ladle is only about 15°–20° C. of the desired mean temperature, which is usually about 1,570°–1,590° C.

Naturally the rate of casting and withdrawal is dependent on the rate of solidification of the steel. The billet must be completely solid before it reaches the flame cutter. This rate of solidification will to some extent be affected by the original metal temperature. As the metal temperature decreases, other conditions being constant, the rate of solidification, and hence withdrawal, can be increased. When keeping within a fairly narrow temperature range, however, as indicated above, the depth of solid skin can be determined from the formula :—

$$D = k\sqrt{T}$$

where D is the skin thickness in inches.

k is a co-efficient which depends largely on plant design, rate of cooling, degree of superheat on the metal, etc., which must be ascertained for each particular plant.

T is the time of contact in minutes.

This formula allows the safe rate of withdrawal to be calculated fairly accurately.

In most of the larger plants, the metal passes through a tundish on its way from the ladle into the water-cooled mould. Generally this tundish is fitted with refractory nozzles, which require frequent replacement. At one plant which the author visited, where there is a four strand continuous casting machine, the metal is lip-poured from a " tea-pot " type ladle, which is provided with a refractory lined lid, into a primary tundish from which it overflowed, as shown in Fig. 4, into two secondary tundishes. These secondary tundishes each feed two strands of the machine, the metal flowing over lips provided at either end of the tundish. Mechanism was provided so that the tilting of the ladle, the control of the primary tundish and the maintenance of the desired level of metal in the moulds could be regulated by one man.

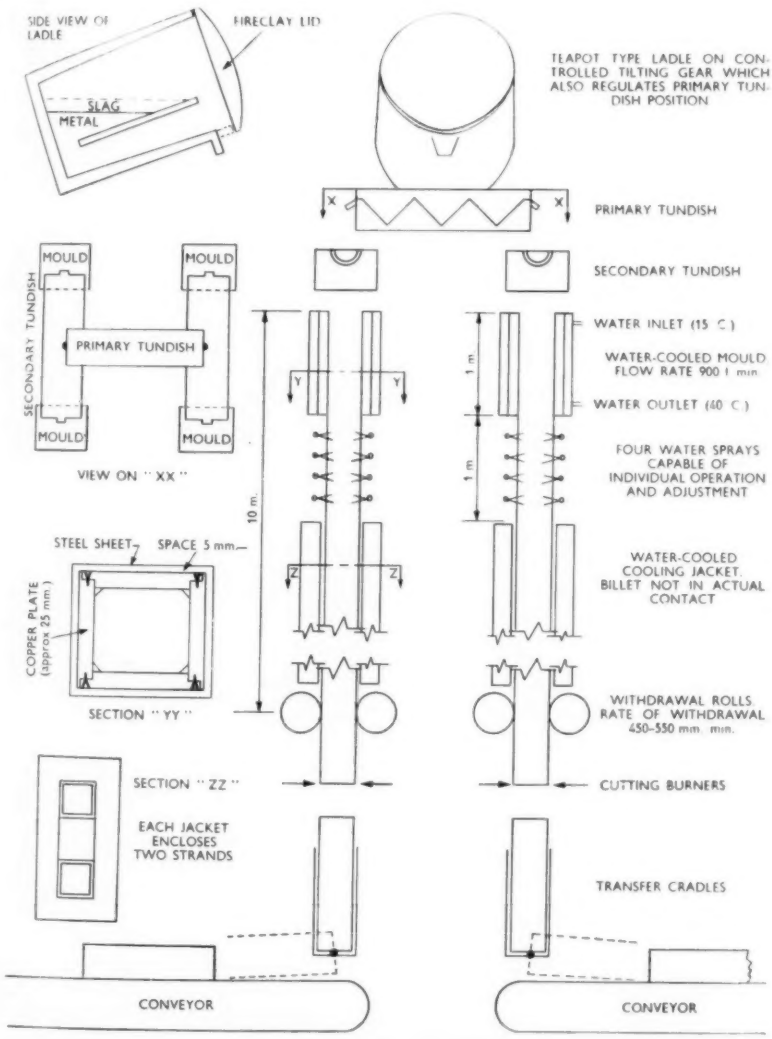


Fig. 4 —The author's impression of a continuous casting machine.

The water-cooled moulds are usually constructed of copper plates, about 1 in. thick, fastened together to form the desired shape. This copper mould is surrounded by a water jacket, which is built up of steel plates. The space between the copper mould and the steel plates or outer jacket must be of sufficient size to allow an adequate flow of water to ensure effective cooling.

There is considerable friction between the mould and the billet during its withdrawal. In order to overcome the destructive action of this friction several attempts have been made to use lubricants. The various methods tried have ranged from the simple expedient of pouring oil into the mould with the molten metal to injecting solid lubricants through the mould walls by mechanical means. The employment of metallic and other types of coating have been investigated. At one plant known to the author, no lubricant is used, except that the mould is painted with graphite prior to commencing to cast. In this case the mould oscillates.

One of the distinctive features of the Junghans continuous casting process is the use of a reciprocating mould, the oscillation of which is mechanically linked

with the speed of the withdrawal rolls. For a short time the mould moves downwards at the same speed as the withdrawal rolls and after a certain distance of travel it returns to its upper position at three times that speed. This oscillation results in practically no motion between the mould and the billet for about 75% of the casting cycle, thereby reducing the erosion of the mould.

Although continuous casting machines are operated in conjunction with open hearth furnaces, there is a preference for the employment of electric furnaces as the melting media. The electric furnace affords a higher degree of process control. A wide range of steels has been cast in this manner, but perhaps fewer problems arise with high carbon and alloy steels. Low carbon qualities necessitate a higher initial casting temperature, which may introduce production problems and quality troubles.

There appears to be some difference of opinion regarding the shapes which can be successfully cast. At one plant they were strongly opposed to casting rounds, and the normal commercial practice was the production of large blooms, about 9 in. square for re-rolling. At other plants, however, the standard products are rounds, especially where alloy steels are being made. In some cases the ovality of the rounds is very obvious.

The author has examined many specimens of continuously cast material. In most cases sulphur prints and macro-etchings showed that the steel was free from surface defects and central porosity. In certain circumstances central porosity may be very pronounced, and there are occasions when isolated blowholes are present beneath the skin.

Discussing the quality of continuously cast material with people engaged in its production, it would appear that three main types of defect can been countered :—

(1) Segregation and central porosity : segregation is largely associated with metal cleanliness and can be corrected by adjustment to the steelmaking practice ; central porosity is a function of the initial casting temperature and the rate of withdrawal.

(2) Surface and subcutaneous blowholes, which appear more peculiar to the lower carbon grades, and can be avoided by correct deoxidation practice.

(3) Intercrystalline segregation which occurs occasionally just within the columnar crystal zone. This type of defect appears to be caused by quenching too rapidly in the water spray or secondary cooling stage, and can be largely prevented by the careful control of chilling at this point.

The author feels that the control of central soundness is perhaps one of the more serious problems associated with continuous casting. The quality of continuously cast products is ideal for rolling or further mechanical working. He feels that further rolling or mechanical treatment is essential to overcome the possibility of central looseness and to refine the " as-cast " crystalline structure.

The output of many continuous casting machines is limited by the melting facilities available. A four strand machine should be capable of casting 40 tons per hour, and allowing a further hour for the necessary preparation, should be capable of producing 480 tons a day, which is approximately 125,000 tons per annum. At any steelworks where the melting shop and small mill capacity exceeds that of the cogging mill, the installation of a continuous casting machine merits serious consideration. The economics of such an innovation would appear to be favourable.

An excellent description[2] of the continuous casting plant at the Cail works in Denain, France, has appeared recently in the technical press. At this most interesting works, which is chiefly engaged in heavy engineering and employs some 3,000 workers, they produce heavy castings and forgings, and also roll sheets varying from 24 gauge to $\frac{1}{8}$ in. thick. In addition to the melting units, foundries, forges, small rolling mills and heat treatment shops, they have two twin-strand Junghans-type machines for continuously casting 240 mm. square bars at a rate of 475–575 mm./min. These squares are subsequently rolled in the small mills into sheets. A large percentage of the sheet production consists of deep-and extra-deep-drawing qualities and electrical qualities for dynamo and transformer work.

Iron and Steel in Holland

The trip concluded with a visit to the Royal Netherlands Blast Furnaces and Steelworks at Ijmuiden, Holland. The author, perhaps like many others equally ill-informed, had visualised a comparatively small plant, but was quickly disillusioned. Not only was he impressed by the size of the works, but more especially by the carefully planned layout enhanced by several beneficial natural features and the efficient organisation and administration. One very interesting feature is the excellent waterway and railway communications.

The works owns an outer harbour with direct connection with the North Sea, whereby ocean-going vessels can bring iron ore from North and West Africa, France, Spain, Canada, and South America, adjacent to the blast furnace plant. In a similar manner some of the coal required is imported from U.S.A. The average depth of this harbour is about 30 ft., with a tidal variation of only about 5 ft. Further supplies of coal are brought either by barge or by railway from Western Germany, Belgium or the Limburger coalmines of Southern Holland. Limestone is delivered either by railway or by inland waterway.

The coke required for the blast furnaces is produced in a by-product coke oven plant capable of a daily output of 1,800 metric tons. In 1956 this plant produced some 7,000,000,000 cu. ft. of gas, and the greater part of the purified gas was sold to the municipalities of the North Holland province for domestic and industrial use, Amsterdam consuming the largest portion.

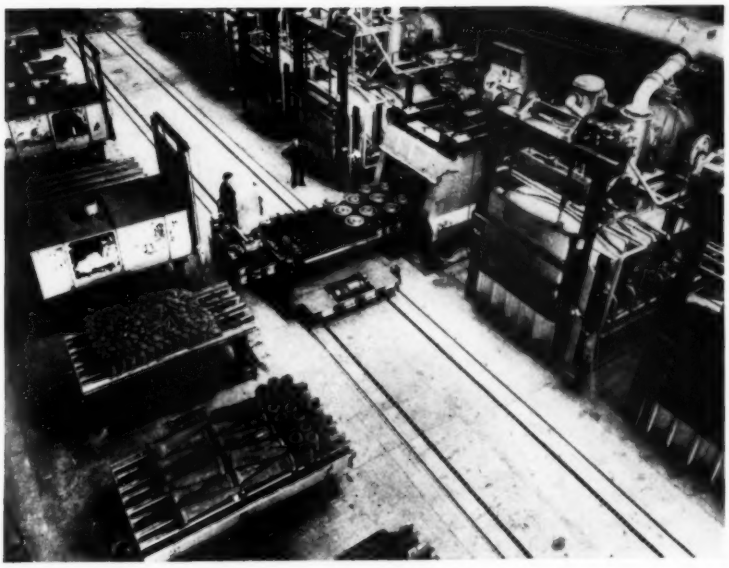
The blast furnace plant consists of four furnaces and has a potential output of 1,000,000 metric tons per annum. The pig iron is transferred from the blast furnaces in mixer-type hot metal cars either to the steelplants or to the pig casting machine. The greater part of the hot metal is consumed in their own steelmaking units, whilst some of the cold pig iron is used in their pipe foundry, the rest being sold to other steelworks and foundries in Holland and abroad.

The open hearth melting shop consists of six 200 ton fixed furnaces having a potential output of 800,000 metric tons per annum. The latest addition to the steelmaking units is a top-blown converter plant capable of an annual output of 300,000 tons, bringing the total steel production up to 1,100,000 metric tons per annum. A large percentage of the output is rimming steel for the production of plates, sheets and strip.

(*Continued on page* 142)

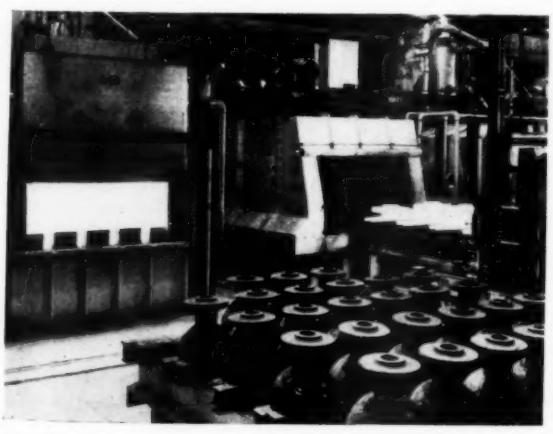
Heat Treatment of Stampings

New Plant at Darley Dale



General view of the new heat treatment department. The rotating charging machine is withdrawing a batch of turbine discs from the oil quenching machine. The furnaces are located on the far side of the charging machine track, with the loading tables, slow-cooling chambers and forced air cooling table on the near side.

WHEN the Darley Dale Works of The Firth-Derihon Stampings, Ltd., were built in the 1941/42 period, conditions then operating necessitated the installation of a coke-fired producer gas plant to operate in conjunction with producer gas-fired forge reheating and small batch type heat treatment furnaces. These operated satisfactorily up to 1956, when the need for much greater accuracy in the heat treatment procedure to deal with the whole range of the highest quality alloy and carbon steels, nickel-alloys and titanium alloys, together with increasing maintenance requirements of the gas producer plant, brought about the decision to change over to the use of town's gas for all furnace firing, and to modernise the furnace equipment. The first stage in the modernisation programme was the laying of a 12 mile long × 15 in. diameter high pressure town's gas main from Chesterfield, via Matlock, to the Darley Dale Works; the installation of a new high capacity town's gas meter and governor house; and extensive modification of the internal distribution gas main.



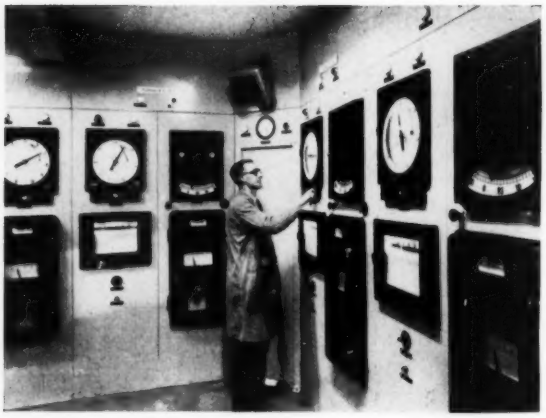
Gas turbine discs being transferred from a dual-system furnace to the oil quenching machine

Whilst the Darley Dale and Tinsley Works had previously been responsible for the heat treatment of their own production, it was decided to install a complete new heat treatment plant at the Darley Dale Works, capable of handling the whole of the heat treatment requirements of the Company and to concentrate all heat treatment at these works. The commissioning of the new central heat treatment plant, which is comparable with any installation in Europe, has meant a reduction of 50% of the labour force previously employed on heat treatment, and also a reduction of 75% in the maximum number of heat treatment furnaces in operation.

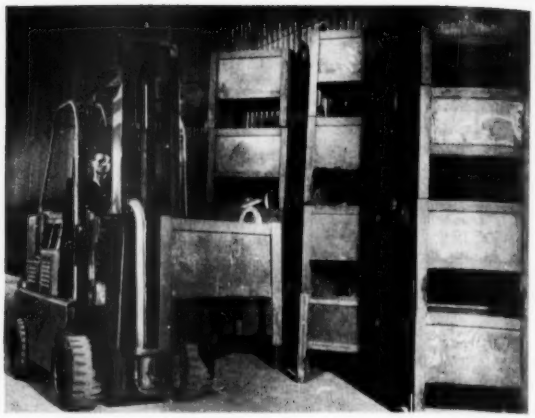
The new plant which incorporates many advanced ideas was designed jointly with Messrs. Gibbons Bros. Ltd., Honeywell Brown, Ltd.,* Hartons Ltd., and members of the staff of the Brown-Firth Research Laboratory. It comprises three Gibbons dual-system heat treatment furnaces, two Gibbons tempering furnaces, a centralised waste gas discharge system, a Gibbons oil quenching machine, a Gibbons-Van Marle turntable charging machine, loading and cooling tables, and an instrument control room.

All furnaces are 11 ft. long, ×6 ft. 6 in. wide and have a height of 3 ft. 3 in. to the spring line of the doorway arch. Loads up to 5 tons weight can be treated in each furnace. The dual-system furnaces have normal operating temperature ranges of 200–750° C. with forced recirculation, and 750–1,250° C. without forced recirculation, whilst the tempering furnaces have normal operating temperature ranges of 200–750° C. with forced recirculation.

* Now Honeywell Controls, Ltd.



A view of a section of the interior of the air-conditioned instrument room.



A 6,000 lb. capacity Conveyancer diesel-engined fork-lift truck moving a stillaged load of forgings.

Furnace temperatures are electronically controlled by a fully automatic electro-pneumatic system, the Honeywell-Brown control instruments being housed in a centrally positioned air-conditioned instrument control room. The tempering furnaces are two-zone controlled and the dual-system furnaces single-zone controlled. Temperature distribution throughout the furnaces is held to extremely fine limits, and is indicated and recorded at any six points in each furnace.

All furnaces are fully instrumented and controlled to safeguard against failure for any reason. Compressed air supply for operation of the pneumatic control equipment is obtained from duplex air compressors and receiver units mounted on top of the centrally sited instrument control room, and the actuation of the air compressor units is automatically controlled via the instrument control room. Kent gas-flow recorders are used to record gas-flow rates and total gas consumptions of each furnace. All waste gases from the furnaces are collected through a centralised overhead waste gas main and then discharged into the atmosphere via a high capacity waste gas exhaust fan and chimney stack.

The oil quenching machine is of advanced design, being of the fully enclosed type with automatic door operation. Automatic lowering and lifting of the load with variable-controlled oscillation of the load during the quench period is also incorporated. This ensures the optimum oil flow conditions during the quenching cycle. For cooling the oil in the quench machine, it is drawn from the top of the tank, passed through a water-cooled oil cooler, and returned to the tank via distribution ducts in the tank base. The oil cooler is capable of dealing with 27,000 gallons of oil per hour, using 12,000 gallons of water per hour. Oil temperature is shown by an indicator on the discharge pipes from the oil tank.

The charging machine used in conjunction with the loading tables, furnaces and oil quench machine is an all-electric, four-arm turntable design arranged for 5 ton loads. Four motors are used for hoisting, lowering, charging and discharging, traversing, and rotation. Power is supplied to the charging machine via a specially designed motorised cable-drum unit, mounted on the charging machine, the feed cable being laid in a small duct below floor level.

The general layout has been designed to handle large and small batch production efficiently and to eliminate manual handling, as the plant has to deal with a wide range of forgings varying in weight from a few ounces up to about 800 lb. All incoming materials enter the reception bay in stillaged form ; diesel-engined fork-lift trucks and electric battery-operated stillage trucks being used for the movement of all stillaged loads into the storage area, between the storage area and the loading tables, and, after treatment, into the adjacent inspection department.

In the main heat treatment bay, electric overhead cranes are used for assembling the heavier forgings on the loading tables, etc. Dependent on the weight and section of the forgings to be treated, they are loaded into special heat-resisting furnace trays or onto heat-resisting bearer-bars. After the load has been assembled on the loading table it operates as a unit load throughout all subsequent operations in the heat treatment department.

Some Impressions of the Continental Steel Industry (*Continued from page* 140)

The ingots are cogged into slabs, varying from 4–8 in. thick, in a two-high reversing slabbing mill, which is driven by a 6,000 h.p. motor. Part of these slabs are converted, after reheating in continuous furnaces, into plates in a two-high roughing stand and a four-high finishing stand. In 1956 more than 260,000 metric tons of medium and heavy plates varying in thickness from 4–35 mm. were rolled. In some cases heavier plates were produced. The bulk of these plates are consumed in the Dutch shipbuilding industry. The works also possess a hot wide strip mill, a cold reduction wide strip mill, cement and chemical works. The continuous pickling line is of particular interest, whilst the final inspection bays leaves little, if anything, to be desired.

Acknowledgments

The author would take this opportunity of thanking all those people, too numerous to mention by name, who made this trip so interesting and informative. He is deeply indebted to them for the valuable time they devoted to him and the information they were always ready to impart.

1 Three Years L-D Steel Voest. Vereinigte Osterreichische Eisen-und Stahlwerke A.G. Linz, Austria, 1956.
2 Fievet. *Journal of Metals*, September, 1957.

NEWS AND ANNOUNCEMENTS

Institute of Metals Meeting

THE Golden Jubilee Autumn Meeting of the Institute of Metals will be held in Birmingham from Monday to Friday, September 22nd to 26th. The location is particularly appropriate, as the first Autumn Meeting of the Institute was held in that city. The headquarters of the Meeting will be the new College of Technology at Gosta Green, where, on Tuesday morning, Mr. G. L. Bailey, C.B.E., will deliver the Twenty-Ninth Autumn Lecture on "Fifty-Years' Progress in Non-Ferrous Metals Technology." Technical sessions on Wednesday and Thursday mornings will be concerned, respectively, with extrusion and dislocations. At the former, five papers will be presented for discussion, whilst the latter will take the form of a review of the history of dislocations and the experimental evidence for their existence, illustrated by four films.

The Birmingham Local Section of the Institute has arranged an attractive programme of works visits and social functions, which will include a civic reception and a banquet at the Kynoch Works of Imperial Chemical Industries, Ltd., Metals Division.

Post Graduate Courses in Metallurgy

Two short post-graduate courses are being organised by the Department of Metallurgy in the College of Technology, Gosta Green, Birmingham during the Autumn Term.

The course on "Nuclear Power Materials" is intended for technical staff engaged in research and development on nuclear reactors, and for students proceeding to advanced metallurgy examinations. Ten lectures will be given on successive Tuesday evenings, commencing on October 7th, 1958. Extraction, fabrication and physical properties of the fissile metals and of those non-fissile metals of special interest in reactor technology will be dealt with, together with the effects of radiation. The development of fuel elements and canning materials will be reviewed, as will the metallurgy of reactor structural work.

The course on "Spectrographic and Chemico-Physical Analytical Techniques for Metallic Materials" is intended for metallurgists and chemists engaged in research and development work. Subjects to be dealt with include spectroscopy and its application to both ferrous and non-ferrous alloys, polarography, absorptiometry, and the established electro-chemical methods. The course will consist of twelve lectures, held on successive Wednesday evenings, commencing on October 8th, 1958.

The fee for each course will be two guineas, and full details of each programme, together with application forms, can be obtained from the Department.

Factual Film Sources

A COMPREHENSIVE guide to sources of informational films, which should be of particular interest to secretaries of technical societies and readers concerned with the use of films for educational purposes, appeared in the August issue of *Film User*. While they last, free copies may be obtained in response to bona-fide enquiries to the office of *Film User* at 319 High Holborn, London, W.C.1. The September issue of the journal will feature an index to film subjects, showing the sources from which films on particular subjects may be obtained.

Steelworks Cranes Study

STEELWORKS cranes will be the subject of the 37th Meeting of the Iron and Steel Engineers Group of The Iron and Steel Institute, which is being held in Chester from October 14th to 16th. The first day's discussions will centre round the crane in relation to the man who operates it, and in the second technical session the steelworks crane will be discussed from an engineering viewpoint.

In addition to the two technical meetings, there will be an all-day visit on October 15th to the Irlam Works of the Lancashire Steel Manufacturing Co., Ltd., followed by a dinner in Chester by invitation of the Company. Further details may be obtained from the Secretary, The Iron and Steel Institute, 4 Grosvenor Gardens, London S.W.1.

Borough Polytechnic Courses

DURING the forthcoming Autumn Term, the Borough Polytechnic, Borough Road, London, S.E.1 is offering a course of lectures on "Modern Developments in Metal Finishing," which is designed to provide a detailed and up-to-date survey of some selected methods of metal finishing and related topics. In addition to technological aspects, the course will deal with human relations in the plating industry, and with costing. The lectures will be delivered on successive Wednesday evenings at 7 p.m., commencing on October 8th, 1958. The fee for the course is £1 : further particulars can be obtained from the Principal.

The Polytechnic is also running a number of courses on fuel technology in preparation for the City and Guilds examinations and the Higher National Certificate Course in Mechanical Engineering. There will also be a course on Friday afternoons on oil burning technology.

Nickel Alloy Exhibitions

A SERIES of four-day exhibitions devoted to the practical uses of nickel and its alloys are to be held in Newcastle, Leeds and Belfast, during September and October by Henry Wiggin and Co., Ltd. The first will be at the Royal Station Hotel, Newcastle upon Tyne from September 23rd to 26th : the second at the Metropole, Leeds, from October 14th to 17th : and the final one in this series will be from October 28th to 31st at the Grand Central Hotel, Belfast.

Running concurrently with each exhibition will be a series of lectures and film shows demonstrating the practical uses of Wiggin alloys in high temperature work, and in chemical and electrical engineering, and others will feature welding techniques, each using one or more of the alloys, to show how all industries take practical advantage of the special characteristics.

Tickets for each exhibition are available from the local area office of Henry Wiggin and Co., Ltd., or direct from the head office at Wiggin Street, Birmingham, 16.

Heating Element Agreement

THE GENERAL ELECTRIC CO., LTD., has recently extended its range of process heating equipment following agreements entered into with Metallwerk Plansee G.m.b.H., of Reutte, Tyrol, Austria, in connection with the production and operation of high vacuum arc melting furnaces for the melting of refractory or rare metals such as molybdenum, tungsten, tantalum, titanium, zirconium, thorium, uranium, etc., and also in connection with the production and operation of electric furnaces with incorporated heating elements of molybdenum, tungsten and/or tantalum, with or without screening and radiation sheaths of molybdenum or other materials. Elsewhere in this issue is an article by R. Kieffer and F. Benesovsky of Metallwerk Plansee G.m.b.H., dealing with the use of these materials as metallic heating elements for high temperature furnaces.

Course on Ternary Systems

A COURSE of eight tutorials on "Ternary Systems in Metallurgy" will be held at the Northampton College of Advanced Technology, St. John Street, London, E.C.1, on Thursday evenings at 6.30 p.m., commencing on October 23rd, 1958.

The lecturer will be Mr. F. B. Elliott, and the syllabus will cover the construction of ternary models and diagrams and the interpretation of the cooling of typical ternary alloys. Opportunity will be given for the discussion of specific cases in which members of the tutorials may be interested. The fee for the course is £2 2s.

Personal News

MR. G. R. BASHFORTH is retiring from the Round Oak Steel Works, Ltd., at the end of September after having served the Company for 31 years. Mr. Bashforth joined Round Oak as Assistant Melting Shop Manager in 1927, became Melting Shop Manager in 1938. In 1955 he was appointed Chief Technical Liaison Officer. Mr. Bashforth hopes to devote more time to writing, lecturing and consulting work: he is also joining Coalmoor Refractories, Ltd., in a technical and sales capacity.

MR. R. J. BARRITT has been appointed Chief Executive, Engineering Division, The British Oxygen Co., Ltd.

MR. R. T. HAYES has been appointed a Director of United Coke and Chemicals Co. Ltd., a subsidiary of The United Steel Cos., Ltd. Mr. Hayes, who joined the United Steel Group in 1946, is Commercial Manager of United Coke and Chemicals, and of United Steel's Ore Mining Branch and the Santon Mining Co., Ltd.

MR. J. COLLINS, Commercial Manager of the Liverpool and Netherton Works of the English Electric Co., Ltd., has been elected Chairman of the Mersey and North Wales Centre of the Institution of Electrical Engineers for the 1958/59 session.

THE British Aluminium Co., Ltd., announce that MR. P. T. ENSOR, formerly General Manager of the Canadian British Aluminium Co., Ltd., has now returned to the United Kingdom and has been appointed Assistant to the Commercial Director, Mr. G. W. Lacey.

CONSEQUENT upon the formation of Brayshaw Furnaces, Ltd., and Brayshaw Tools, Ltd., Mr. F. I'ANSON, Sales Manager of the Furnace Division, will continue to control home and export sales of Brayshaw Furnaces, Ltd., whilst Mr. W. NUNN, formerly Export Sales Manager of the Tools Division, is appointed Home and Export Sales Manager of Brayshaw Tools, Ltd.

THE Steel Company of Wales announces that MR. I. S. SCOTT-MAXWELL, who has been unable to carry out his duties for an extended period due to illness, has now returned to full time duties as Assistant General Manager (Engineering and Development) of the Steel Division of the Company. At the same time the Company confirms the appointment as Chief Engineer of MR. J. H. GROOCOCK (formerly Chief Electrical Engineer) who, in the absence of Mr. Scott-Maxwell, has been carrying out the duties of Acting Chief Engineer. MR. H. D. MORGAN, who, during the same period has been Acting Chief Electrical Engineer, is now appointed Chief Electrical Engineer.

MR. G. H. WALTON, Joint General Manager with MR. O. J. CROMPTON of British Insulated Callender's Construction Co., Ltd., has relinquished his executive duties on reaching retirement age. He continues to be available for consultation and for special duties as may be required. He remains on the Board of the Company and also of British Insulated Callender's (Submarine Cables), Ltd., Painter Bros., Ltd., and Engineering Projects, Ltd. Mr. Crompton has been appointed General Manager and MR. G. A. RENDLE Deputy General Manager: Mr. Rendle continues to act as Manager of the Power Cable and Telecommunication Cable Contracts Departments. MR. E. T. Q. DAVIES has been appointed Director and continues to act as Manager of the Overhead Line Contracts Department. At the end of June, MR. F. B. KITCHEN retired from the Board and relinquished his Directorship of British Insulated Callender's Cables (Australia) Pty., Ltd.

BRITISH OXYGEN have announced the award of three Fellowships for postgraduate research. The awards have been made to MR. P. G. CLAY, of King's College, Newcastle upon Tyne, for research in the Department of Chemistry at the College; MR. R. E. RAAB, of the University of Natal and the University of Oxford, for research work in the Physical Chemistry Laboratory at Oxford, and MR. G. SAVILLE, B.A., of the University of Oxford, for work in the Inorganic Chemistry Laboratory at Oxford. Renewal of Fellowship for a third year has been granted to MR. N. G. PARSONAGE, for work in the Inorganic Chemistry Laboratory at Oxford University.

MR. C. S. WILKINSON, at present Manager of the Templeborough Finishing Banks at the Steel, Peech and Tozer Branch of United Steels, will move from this appointment for attachment to the Superintendent of Rolling Mills at the Branch until the end of the year. On January 1st, 1959, he will become Manager of the Brinsworth Mill. MR. E. RYDER became Manager of the Templeborough Finishing Banks on August 1st, 1958, with MR. G. H. SAMBROOK as Assistant Manager.

BRITISH INSULATED CALLENDER'S CABLES, LTD., announce the appointment of MR. O. W. MINSHULL to be General Manager of its Power Cables Division. He will remain Deputy Chairman of British Insulated Callender's Construction Co., Ltd., and a Director of British Insulated Callender's (Submarine Cables), Ltd.

MR. P. S. BEALE has been appointed a Director of The British Oxygen Co., Ltd. Mr. Beale was formerly Chief Cashier, Bank of England, and recently General Manager of The Industrial Credit and Investment Corporation of India, Ltd., Bombay.

RECENT DEVELOPMENTS

MATERIALS : PROCESSES : EQUIPMENT

Treatment for Residual Fuel Oils

A NEW treatment for residual fuel oils, low viscosity fuels, distillates and coal tar fuel, has been introduced by the Amber Chemical Co., Ltd. The treatment, in the form of a liquid additive known as Amber SSR511, acts to minimise the formation of sludge, by retarding the rate of oxidation occurring in stored fuels, and by dissolving the resins, asphaltenes, gums and congealed residual oil which are the main constituents of sludge.

The formation of sludge is a frequent indirect result of modern refining technique, which tends to remove a high proportion of the volatile fractions, leaving the residual fuel correspondingly lower in quality. Some chemical reaction or oxidation of the fuel may occur in storage prior to combustion—a process which is increased by the application of heat and the presence of water. It may be accelerated by minute amounts of metallic compounds, such as copper, (probably derived from the fuel system). The resulting oil insolubles, having a high carbon content, can seriously affect combustion and cause blockages which may lead to repeated overhauls, or a complete stoppage. Amber SSR511, which possesses a greater solvent power than the oil itself, will dissolve the greater part of this sediment before it reaches the burners and will act to inhibit the oxidation process in the fuel storage tank. The additive is completely soluble in the oil, and its action is not affected by the presence of water. It is non-corrosive and non-volatile, and as it has a high flash point, it is safe to store and handle.

The cost of treatment using Amber SSR511 is approximately 0·06d. per gallon of fuel consumed.

The Amber Chemical Co., Ltd., 11a Albemarle Street, London, W.1.

Pipeline Welding Machine

A NEW development which, it is claimed, will speed up the process of pipeline welding on site, has been made by Quasi-Arc, Ltd. It is a pipe double-ending installation, which enables two 30–40ft. lengths of pipe to be welded together automatically, after which the double length is joined to the pipeline by conventional manual stove-pipe welding methods. The manufacturers maintain that a considerable saving in time can be effected and that the versatility of the machine is likely to bring it into wide use in the oil industry.

The length of the pipe is supported on two idler units, each of which incorporates six ball castors arranged in V-formation. This method of mounting not only enables the pipe to be rotated for welding, but also allows it to be withdrawn in the longitudinal direction. It also means that pipes of 6 in. to 38 in. in diameter can be accommodated without any adjustment. The two pipes to be butt welded are loaded on to the idler units with their ends butting together, and are rotated by two pairs of large diameter rolls, each pair being driven by a ½ h.p. motor. The two motors are supplied with D.C. from a motor-driven generator with Ward-Leonard control, and reduction gearing enables the welding speed to be varied from 7 to 70 in./min. Pipes between 6 in. and 26 in. in diameter can be rotated without any adjustment to the height of the drive rolls, and only slight adjustment of the rolls is needed to engage and disengage the pipe. This adjustment is operated by a handwheel rotating a leadscrew with right- and left-hands thread to move both carriages simultaneously. Slight variations in loading are taken up by thick rubber tyres on the rolls.

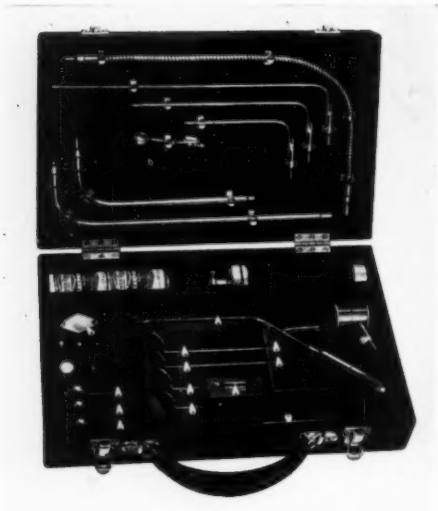
The vertical frame on which the welding head carriage runs forms a single integral unit with the roller bed frame, and is of simple construction. The arm carriage is raised and lowered manually, the arm being counterbalanced, and can be clamped at any desired height. The welding head, Fusarc CO_2, Fusarc or Unionmelt, can be adjusted to the required position relative to top dead centre of the vessel and clamped, and has the standard vertical and traverse slides for fine adjustment.

Quasi-Arc, Ltd., Bilston, Staffs.

Industrial Inspection Kit

THE basis for the new Ellispection kit for industry is provided by the optical equipment used by the medical profession for the examination of the eyes, ears, nose, throat and other portions of the body, with its probes, mirrors, miniature electric lights, etc. The adaptation and application of this equipment to the needs of industry has made it possible to illuminate and inspect the most inaccessible spot through the almost impossibly small aperture. The Ellispection kit comprises a series of rigid and flexible probes with fixed and movable mirrors, magnifiers and midget battery operated electric lights, the smallest being ⅛ in. in diameter. All parts are interchangeable and interlocking, thus, one or more parts in any combination, make it possible to probe, illuminate and inspect machinery, castings, dies, pipe assemblies, chemical plants, electronic valves and many other types of plant or equipment.

As will be seen in the illustration, the compact kit is housed in a fitted, black hardwood case, which is both compact and easy to carry. All metal parts are finished



in durable nickel and two standard U.2 type torch batteries, or their equivalent, which are readily obtainable, provide the necessary electricity and are housed in the battery handle. Spare bulbs and spare batteries are supplied with each kit.

Ellis Optical Co., Mayday Road, Thornton Heath, Surrey.

Pencil for Glazed Surfaces

A NEW-TYPE blacklead pencil which writes on plastic, china, glass, and all glazed surfaces is being marketed by the Plastic Packaging Division of Gordon & Gotch, Ltd. Known as the Swan All-Stabillo, this new pencil writes clearly and densely on films, plastics, glass, metal, porcelain, stone, leather, foils, rubber, transparent wrappings, or art and glossy paper, and its exceptionally black density is ideal for photo copying. Non-dusting and waterproof, it is removed from paper with a pencil eraser and from other surfaces with a damp cloth. It can be used equally well as a normal pencil, requiring less resharpening than softer wax-type pencils.

The Plastic Packaging Division, Gordon & Gotch, Ltd., 75–79 Farringdon Street, London E.C.4.

Arc-Welding

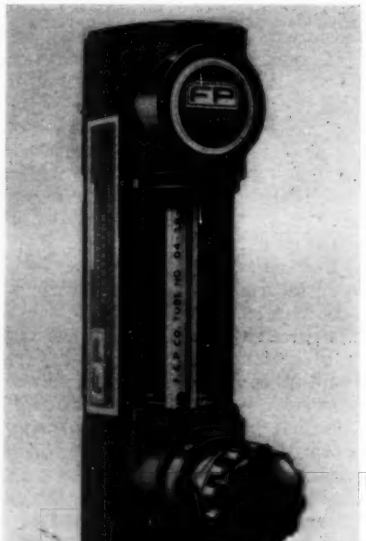
QUASI-ARC, LTD., have recently introduced a range of new low voltage safety devices for use with A.C. arc-welding plant. The function of the device is to reduce the relatively high open circuit voltage to a safe value. It is possible for electric shock to occur from accidental contact with live parts of welding equipment such as electrode holders. The effect is not serious under normal conditions but there are circumstances, such as when working at heights or in cramped spaces or in wet surroundings, where it could be hazardous. A device to obviate risk when using A.C. current in these conditions is advocated in the Memorandum on Electric Arc-Welding issued by the Factory Department of the Ministry of Labour and National Service.

A low voltage safety device, however, should not be detrimental to welding performance or to the natural characteristics of the welding set. If it makes arc striking difficult, or is so sensitive that it operates with fluctuations of the arc, an operator may be tempted to discard the entire arrangement. Three versions of the new device have been produced for single and multi-operator sets, and the principle of operation is the same in each case. They effectively reduce the open circuit voltage from 80 or 100 to 30 volts, and speed of response when striking an arc is such that even an experienced welder cannot detect the presence of a device. At the same time, normal fluctuations of the arc do not cause the device to operate, since the circuit incorporates a preset time delay. Correct operation of the device is indicated by a small low voltage neon lamp which is illuminated when the set is on open circuit at the reduced voltage. The lamp is extinguished when welding is in progress, or should a failure occur in the device when the set is on open circuit.

Quasi-Arc, Ltd., Bilston, Staffs.

Flow Control

FISCHER AND PORTER, LTD., announce the addition to their flowmeter range of Models 1115 & 1120 Purgerator Meters. Although completely new in the United Kingdom, the F & P Purgerator is widely used in the U.S.A. The new model is an inexpensive reduced-accuracy indicating variable-area flowmeter, produced primarily for controlling the flow of gases and liquids at a constant rate for bubbler service applications and purging operations, as with corrosive service manometers. Additionally, it is used in conjunction with the F & P constant differential pressure regulator for measuring liquid level in an open tank, and for other diverse applications where a small flow-indicator is required. The meter body, which measures approximately $5 \times 1\frac{1}{4}$in. is manufactured from corrosive-resistant, black phenolic plastic, and is available with (Model 1115), or without (Model 1120) an integral 18/8/3 stainless steel needle valve. The metering tube is of borosilicate glass, and



may be scaled in any desired units of flow for 10 to 1 ranges, from 0·08–0·8 cc./min. air to 142–1420 cc./min. water and 3,820–38,200 cc./min. air.

Fischer and Porter, Ltd., Salterbeck Trading Estate, Workington, Cumberland.

Earth Lead Tester

SOME fifty people are killed each year as a result of defective earthing systems on portable electric tools and appliances, and many more have sustained injuries of varying seriousness. Gresham Transformers, Ltd., are now marketing an earth lead tester for 240 volts, 50 cycles, single-phase supplies, in the development and testing of which the company has had the benefit of close collaboration with H.M. Inspectors of Factories.

The instrument makes its rapid test by ascertaining the continuity and adequacy of the earth lead of the tool or appliance, the supply lead of which is plugged into one of the standard 3-pin sockets (5 amp., 13 amp., or 15 amp.) on the panel. The action is fourfold:

(1) The resistance of the lead before the main test is measured.

(2) The main test; a heavy current of 100 amps. is passed through the lead for two seconds.

(3) The resistance of the lead is again measured.

(4) A mains voltage is applied to the tool or appliance to ensure that it, itself, is in working order.

If the lead is defective to the extent of requiring examination, resistance (3) will be higher than (1). If there is an open circuit, resistance (3) will be infinite. If (1) and (3) are identical, the lead is satisfactory.

Gresham Transformers, Ltd., Twickenham Road, Hanworth, Middlesex.

Choosing Protective Filter Glasses

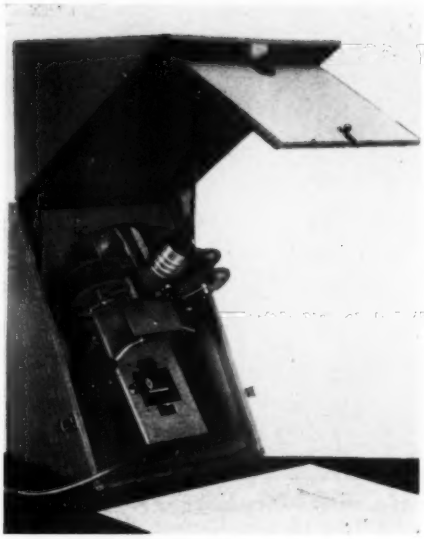
NEW aids to assist welding firms choose the correct types of protective filter glasses for their operatives have been devised by Chance Brothers, Ltd. They take the form of cards and wallets containing samples of seven Protex glasses for electric welding and eight Protal and Protex glasses for gas welding with and without flux. All conform to British standard specifications. With them it is easy to decide which filter is the most suitable for a particular job, by trying out a selection under working conditions. The cards and wallets are available free on application to suppliers of welding protection equipment.

Chance Brothers, Ltd., Smethwick, Birmingham.

Microfilm Reader

THE need for an inexpensive microfilm reader which will also scan microfiche is now met by the V.C. Lexicon Reader, which will read microfiche up to a maximum size of 9 cm. wide and can be fitted with a film carrier to take 100 ft. of full-size 35 mm. unperforated microfilm. It is a compact machine, which takes up when not in use a volume of only 15 × 10 × 11 in. and weighs only 25 lb.

The film carrier for microfilm scanning can be removed and re-fitted very quickly and easily, which facilitates film threading. Transport of the film across the gate is effected by a handle mounted on the carrier, and the image remains in focus whether the film is moving or not. A tensioning arrangement eliminates the need for pressure plates and thus prevents accidental scratching.



The fiche image is projected onto a white opaque screen on the desk and is approximately 15 in. square. A prism attachment is available which enables the image to be projected by finger control onto the screen at any desired reading angle. Magnification is × 16, with a gate size of 2·4 × 2·4 cm. Besides microfilm and microfiche scanning, this equipment can also be used as a filmstrip or slide projector.

Micro Methods, Ltd., East Ardsley, Wakefield, Yorks.

Bright Nickel Plating Process

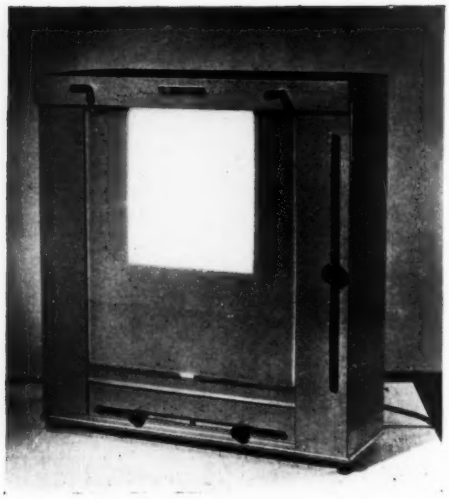
ALBRIGHT & WILSON (MFG.), LTD., are now marketing a new process for bright nickel plating, originally developed in the United States by the Hanson-Van Winkle-Munning Co., where it is known as Nickel-Lume and Levelume. Albright & Wilson have applied for registration of the name Plusbrite for the new process. Major advantages claimed for the new process are the excellent levelling properties provided, together with the fully bright deposit which has a very good degree of ductility. The deposit has an attractive white colour which is also highly receptive to subsequent chromium plating operations where necessary. With the analytical methods available both for the inorganic constituents and the additives, close chemical control of the plating bath is possible at all times.

The process has considerable possibilities in the motor car industry for the plating of a whole range of accessories such as bumpers and over-riders requiring a high standard of brightness and serviceability. The process should also find many uses in the plating of electrical appliances, steel pressings and forgings, zinc-base die castings, and copper and brass parts.

The Metal Finishing Department, Albright & Wilson (Mfg), Ltd., 1 Knightsbridge Green, London, S.W.1.

X-ray Illuminator

THE new Industrex illuminator, Model 2 has been designed primarily for the examination of industrial radiographs with a wide range of densities. The light-



source consists of six 15-watt "colour matching" fluorescent tubes, which provide a brilliant, even illumination of "daylight" quality over the whole area of the screen. This light is sufficiently bright to allow for critical examination of radiographs with densities over 3·5 by full room illumination. Despite the intensity of the illumination, the Model 2 is completely cool in operation, so that the usual ventilation holes are not necessary and, consequently, the illuminator does not collect dust through convection. Because of this absence of heat, the illuminator can be "angled" or let into a bench if required, even in a horizontal position.

An outstanding feature is the masking device which cuts out unwanted light from the viewing screen and operates from 14 × 17 in. down to about 2 × 2 in. The plastic opal viewing screen is extremely robust and can easily be removed for cleaning. Two studs are fitted above the diffusing screen to take the Kodak wet film attachment or to hold hangers containing wet radiographs Dry radiographs are held in position by spring-loaded metal balls located in a metal channel immediately above the illuminated area.

Kodak, Ltd., Kingsway, London, W.C.2.

New Surface Treatment

JENOLITE, LTD., have recently added a new material to their range of chemical pre-treatments for metal surfaces. Recent discoveries in the archaeological field have shown that the presence of vegetable tannins in soil contribute largely to the protection of metal articles buried therein against the corrosive action of bacteria and other hostile agents. This is believed to be due to the formation on the metal surface of a self-sealing coating of tannates, which shields the surface from chemical erosion as well as being resistant to attack by micro-organisms. Advantage has been taken of these characteristics in the formulation of Jenotan, a chemical pre-treatment for metal surfaces, which not only gives protection to underground pipelines and similar structures, but is also of value in other environments where maximum temporary corrosion protection is required, or as a reinforcement to the protective qualities of any subsequent surface coating system.

The Jenotan treatment not only provides a virtually impervious tannate "skin", but also ensures a perfect bond to clean or lightly corroded metal. Application can be by immersion or by brushing, but it is necessary first to remove from all pipelines and, in particular, buried pipelines, all heat scale which may be tightly adherent on the metal substrate.

Jenolite, Ltd., 13–17 Rathbone Street, London, W.1.

Internal Cathodic Pipeline Protection

STEEL pipes carrying sea water corrode internally and the cost of outage time, repairs and replacements is very heavy. Linings are extremely expensive and have not proved a complete answer, since they require constant inspection and with failure they bring the possibility of trouble due to detached portions of the linings obstructing the system. Moreover, any small fault or imperfection in continuity can lead to rapid local perforation.

Sacrificial anodes have been used successfully but are very expensive and difficult to install. Internal cathodic protection has also been used in the past but its application has been limited by lack of suitable anode materials. With the development of CX3 lead alloy anodes, power impressed cathodic protection has become an economical proposition. Unit anodes are inserted in unlined steel pipes, and the protective current is controlled externally so eliminating the necessity of entering the pipe. Conventional potential checks on the efficiency of the system can be made, using special potential measuring pockets which are easily accessible externally.

The system has the additional advantage that the initial capital cost is generally lower than that of existing lining systems, and as associated water storage tanks and condensers may also be tied into the system, protection is given through most of the plant.

Cathodic Protection Control, Ltd., Duncan House, Dolphin Square, London, S.W.1.

Forced Air Circulating Furnace

IN re-designing their electric horizontal forced air circulating furnace, Hedin, Ltd., have improved its performance and simplified its construction, so that in spite of the use of high-grade materials the cost has been kept reasonably low.

The furnace is automatically controlled throughout and includes the latest safety devices. The heat resisting centrifugal type fan is designed to force large quantities of air under considerable pressure through the densest charge and, because the speed and volume of the air flow are both high, there is only a very small temperature variation throughout the heating chamber.

The drive is via a standard V-belt and the fan shaft bearings are air cooled. The door is counterbalanced and can be either hand or mechanically operated, as required.

The furnace is constructed to enable it to stand up to heavy works conditions and maintenance aspects have been borne in mind in its design. Access to the elements is gained by taking out the air guides (a few minutes' work) and replacement can then be quickly effected. Similarly, all bearings are easily accessible for maintenance.

Hedin, Ltd., Commerce Estate, South Woodford, London, E.18.

LABORATORY METHODS
MECHANICAL · CHEMICAL · PHYSICAL · METALLOGRAPHIC
INSTRUMENTS AND MATERIALS
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Ethylenediamine Tetra-Acetic Acid and Allied Compounds in Metallurgical Analysis

By E. G. Brown, A.M.C.T., F.R.I.C.

In this article the author surveys the extensive literature which has appeared in the last few years on the application of Complexones in metallurgical analysis. There is a broad division into ferrous and non-ferrous fields, although a feature of the work in recent years has been that the bulk of the papers published have been concerned with non-ferrous applications.

IN the February and March, 1954, issues of METALLURGIA, the present author described specific proposals that had been published concerning the application of the Complexones (ethylenediamine tetra-acetic acid and allied compounds) in metallurgical analysis. The purpose of the present article is to review the considerable amount of literature published since the initial articles on the subject. As before, only papers dealing with specific metallurgical applications are considered, although it will be realised that many other analytical determinations involving these compounds could probably be applied in metallurgical work. It is believed that the present review is substantially complete in its coverage.

The article is divided broadly into the non-ferrous and ferrous fields. A feature of the work done over the last few years is that the bulk of it is of non-ferrous application; relatively little work has been published in the ferrous field.

The nomenclature using the abbreviation EDTA for ethylenediamine tetra-acetic acid or its disodium salt has become almost standard in this country, and it is proposed to follow this system in the present review, rather than using the term Complexones* originally introduced by Schwarzenbach.

NON-FERROUS APPLICATIONS

Aluminium

Milner and Woodhead[1] determined aluminium in magnesium-base alloys, zinc-base alloys (Mazak) and copper-base alloys, using a volumetric EDTA procedure. In principle, an excess of standard EDTA was added, the solution boiled and cooled; the unused reagent was then titrated with a standard ferric iron solution, using salicylic acid as indicator at *p*H 6·5. In applying the methods to alloys, the aluminium was initially separated as the insoluble benzoate complex. The method was particularly suitable for the rapid routine determination of aluminium in the alloys tested, but some practice was necessary in recognising the end-point. The titration was best applied when the approximate aluminium content of the sample was known.

By using the fact that beryllium hydroxide is insoluble in an alkaline solution of EDTA, Goldberg[2] qualitatively differentiated between beryllium and aluminium bronzes.

Claasen, Bastings and Visser[3] successfully applied the photometric determination of aluminium, described in the ferrous section of this review, to two non-ferrous alloys. These were a phosphor bronze bearing metal containing about 0·04% aluminium and a zinc-base die casting alloy containing about 4% aluminium.

Amin[4] determined aluminium and copper in copper and aluminium alloys such as coinage by the combined use of thioacetamide and EDTA. Copper was completely separated as its sulphide by thioacetamide from a tartrate solution. Excess thioacetamide in the filtrate was then decomposed with nitric acid or potassium persulphate and the aluminium determined by addition of excess EDTA and back-titration with zinc sulphate solution, using Eriochrome Black T as indicator, or with standard thorium nitrate solution, using Alizarin S as indicator. The procedure was applied on a microscale, using a Gorbach micro-burette.

Kinnunen and Merikanto[5] described two procedures using EDTA, for the determination of aluminium in brasses and bronzes. In Procedure 1, the brass or bronze was dissolved in nitric acid and copper was titrated with sodium thiosulphate in the usual manner. A measured excess of standard EDTA solution was then added, together with 0·1g. of ascorbic acid, and the whole boiled to form the aluminium-EDTA complex. Potassium cyanide was now added and the solution made ammoniacal with ammonia. The excess EDTA was titrated with standard manganous sulphate solution, using Eriochrome Black T as indicator; the volume of EDTA used corresponded to the sum of the aluminium, manganese and lead content of the sample. Triethanolamine was now added and the solution boiled. The liberated EDTA, corresponding to the aluminium content was titrated with manganous sulphate as before. Copper, nickel, cobalt and zinc did not interfere in the presence of potassium cyanide. If more than traces of iron were

* The term Complexone is the registered trade-mark of the Uetikon Chemical Company, Switzerland.

present, the procedure failed, and interfering elements had to be removed by mercury cathode electrolysis. This was Procedure 2.

The Dutch workers Detmar and van Aller[6] used EDTA as a screening reagent in the gravimetric determination of aluminium in copper alloys. Aluminium was determined as the oxinate, after precipitation in ammoniacal solution containing potassium cyanide, tartaric acid and EDTA. Copper, zinc, tin, iron, manganese, lead, nickel, and cobalt did not interfere, and 5–40 mg. of aluminium could be determined with a relative error of only 0·5%.

The determination of aluminium in copper-aluminium-iron alloys by Sir and Pribil[7] is noted in the sections under copper and iron.

Beryllium

Goryushina[8] used EDTA for determining beryllium in copper-beryllium bronze by the gravimetric phosphate method. Beryllium was separated from most of the copper, either by electrolysis followed by the addition of a small amount of EDTA to the spent electrolyte to combine with traces of copper, or by direct precipitation of phosphate after the addition of sufficient EDTA to combine with all the copper present. In either method the beryllium was finally determined by heating the beryllium phosphate at 800–850° C. to constant weight. In both methods the error was said not to exceed ±0·02% on a sample containing 2·12% beryllium.

Goryushina, with Archakova,[9] reported on the further use of EDTA as a masking agent in the volumetric analysis of beryllium bronze. Here beryllium ammonium arsenate was precipitated in ammoniacal solution in the presence of EDTA to prevent interference from other elements. The precipitate was then filtered off and the combined arsenic determined therein by iodimetric titration. Under the described conditions of precipitation there was no interference from copper; aluminium could be present in concentrations not greater than 6 times that of the beryllium, and phosphorus could be present when the P_2O_5 : BeO ratio was not greater than 1 : 8.

In the colorimetric determination of beryllium in titanium alloys, Covington and Miles[10] used the tetrasodium salt of EDTA in alkaline solution to avoid interference from magnesium, zinc, copper, nickel, iron and calcium. The interference of titanium was prevented by the combined use of EDTA and hydrogen peroxide. The beryllium was finally determined colorimetrically, using the dyestuff 4-(*p*-nitrophenylazo)orcinol in alkaline solution buffered with borate and citrate. Good results were quoted on synthetic and experimental alloys containing about 0·03–2·0% of beryllium.

Goldberg qualitatively differentiated beryllium and aluminium bronzes using EDTA (see reference 2).

Bismuth

Faucherre and Souchay[11] published a polarographic determination of bismuth in tin-lead solders, no chemical separation being necessary. Interference from tin was prevented by adding EDTA as well as citrate to the base solution, at a final *p*H of 9. Copper was determined simultaneously with the bismuth.

Kinnunen and Wennerstrand[12] presented methods for the determination of bismuth in metallurgical products such as lead concentrates and blister copper. If the bismuth content were very low, a colorimetric method was utilised, otherwise the bismuth was separated off by extraction of the bismuth diethyldithiocarbamate complex with chloroform and, after evaporation with nitric acid, finally titrated at *p*H 6 with EDTA, using pyrocatechol violet as indicator. Alternatively, thiocyanate, thiourea or potassium iodide could replace pyrocatechol violet as indicator in the EDTA titration, using suitable *p*H ranges. An addendum to the above paper[13] detailed precautions to be taken in the photometric procedure.

Underwood[14] determined 0·5–10% of bismuth in simulated lead-tin alloys containing arsenic and antimony. After dissolution in bromine-hydrobromic acid solution, perchloric acid was added and tin, arsenic and antimony volatilised as bromides by heating to fumes. In this solution, bismuth was titrated with EDTA at *p*H 2, following the progress of the titration spectrophotometrically by the disappearance of the yellow bismuth-thiourea complex or the appearance of the blue complex formed by cupric ion with EDTA. Large quantities of lead did not interfere in the determination.

Milner and Edwards[15] used the EDTA titration for the determination of major amounts of bismuth in bismuth-uranium and bismuth-uranium-thorium alloys, the thorium being preferentially complexed with sulphate ions. Pyrocatechol violet was used as indicator in the *p*H range 1·0–3·0.

Shelton[16], in the determination of bismuth in bismuth-uranium alloys, first separated off the uranyl oxinate as described under "Uranium," and then hydrolysed the bismuth-EDTA complex by making the solution alkaline. The precipitated bismuth oxinate was then filtered off and determined gravimetrically. The use of the procedure to determine both bismuth and uranium in the same alloy was best adapted to those alloys in which the bismuth to uranium weight ratios lay between 3 : 1 and 1 : 3.

Cadmium

Kinnunen and Wennerstrand[17] determined cadmium in metallurgical products by appropriate modifications of the zinc thiocyanate extraction method. For cadmium-copper alloys, the nitric acid solution was treated with ammonia and thiourea to complex the copper. The cadmium was then converted to the thiocyanate and extracted with a 1 : 1 methyl ethyl ketone, *n*-butyl phosphate solvent. The cadmium was titrated in the solution with EDTA, after the addition of buffer solution, potassium cyanide, acetone and zinc disodium ethylenediaminetetra-acetate solution, using Eriochrome Black T as indicator.

For substances containing small amounts of cadmium in the presence of large quantities of zinc, e.g. zinc spelter, Kinnunen and Wennerstrand precipitated the cadmium as sulphide in boiling ammoniacal solution with thiourea. The precipitate was then dissolved and treated with hydrochloric acid and ammonium thiocyanate; any zinc was then extracted with a 1 : 4 amyl alcohol, ether mixture. The resulting solution was then treated with ammonia, ammonium hydrogen fluoride and ammonium thiocyanate, and the cadmium extracted with a 1 : 1 *n*-amyl methyl ketone, *n*-butyl phosphate mixture. The resulting solution was then titrated with EDTA as above. The second procedure was suitable for as little as 0·005% cadmium in zinc spelter.

In the photometric determination of cadmium (0·6–1·0%) in copper-cadmium alloys, Nielsch and Böltz[18] separated off cadmium as cadmium sulphide, which was then converted to the cadmium complex of 4-

hydroxy-3-nitrophenylarsonic acid. On dissolution in aqueous ammonia, the cadmium salt was split and the organic compound formed a yellow colour suitable for colorimetry, if interference by cadmium were suppressed by the addition of EDTA.

Cerium

The Czech authors Malinek and Klir[19] described the use of EDTA as masking agent in the analysis of magnesium alloys for cerium content. When cerium was oxidised with hydrogen peroxide in aqueous ammoniacal solution, a yellowish-brown colour developed, suitable for photometric purposes at 400 mμ. The interference of some elements, especially of manganese (even in fifty-fold excess), could be avoided by adding EDTA; nickel, cobalt, copper, tin, titanium, vanadium and uranium interfered, but some of these could be separated by mercury cathode electrolysis.

Chromium

A photometric determination of chromium in bronze was described by the Russian authors Goryushina and Gailis[20]. After dissolution of the alloy in nitric and sulphuric acids and removal of copper by electrolysis, EDTA was added to an aliquot portion of the solution and the solution neutralised to phenolphthalein with ammonia. The solution was then re-acidified with acetic acid, boiled, cooled and the optical density of the resulting solution determined photometrically.

The violet colour obtained in the reaction between chromium^{III} and EDTA had a maximum intensity at *p*H 3–5, and was completely stable for weeks. Citric and oxalic acids interfered; tartaric acid had no effect.

Nielsch and Böltz[21] also reported on the photometric determination of chromium in copper-chromium alloys, measuring the violet complex formed between chromium^{III} and EDTA at 550 mμ. The alloy was dissolved in a nitric, sulphuric, phosphoric acid mixture and heated to fumes of sulphur trioxide. After dilution, 20 mg. of thiourea was added to complex the copper, and then a mixture of sodium acetate and ammonium nitrate to buffer the solution at *p*H 7·5. A solution of EDTA was added, the solution boiled 1 minute and quickly cooled. The whole was made up to 200 ml, an aliquot filtered, and the optical density measured in a filter photometer, using a filter approximating to a wavelength of 550 mμ.

Cobalt

Nielsch and Böltz[22] utilised the deep red complex formed between nitrilotriacetic acid (NTA) and cobalt, showing an absorption maximum at 510 mμ, for the photometric determination of cobalt in cobalt-rich alloys. The optical density of the complex varied with the *p*H, but was constant between 4·9 and 5·7. Acetate and tartrate interfered, and allowance was made for the presence of a constant amount of acetate in the method. No further details are available.

Copper

EDTA was used as a screening agent in the gravimetric determination of copper using 2(*o*-hydroxyphenyl) benzoxazole by Byrn and Robertson[23]. The method was applied to a nickel-copper alloy, an aluminium alloy, a cast iron and a bronze. At *p*H 11, in the presence of EDTA, the reagent was virtually specific for copper when present with other metal ions normally present in the alloys quoted above. The only interferences were those metals precipitated from EDTA solutions at *p*H 11, which could be separated before addition of 2(*o*-hydroxyphenyl) benzoxazole. Special procedures had to be devised in the presence of large amounts of iron and aluminium, using tartrate as an additional masking agent for the iron and precipitating at a *p*H less than 3·5 in the case of aluminium. In general, the procedure was applicable in the presence of nickel, manganese, cobalt, iron, chromium, aluminium, titanium, zinc, tin, lead and magnesium. Good results were quoted for values of copper ranging from 2·48 to 57·39% for the various alloys. The procedure was claimed to be simple, direct and accurate, and the precipitate had a favourable conversion factor.

Cluley[24] used EDTA as a masking agent in the determination of small amounts of copper in metals by the well-known diethyl dithiocarbamate method: iron, cobalt and nickel did not interfere. The metal solution, containing EDTA and an excess of ammonium hydroxide, was treated with diethylammonium diethyldithiocarbamate in chloroform and the coloured extract measured photometrically. In the non-ferrous field, the method was applied to an aluminium alloy B.C.S. 181 (4·64% Cu) and a white metal B.C.S. 177 (0·33% Cu).

Bismuth was the only element interfering in Cluley's method. Under these circumstances, the total photometric absorption due to copper plus bismuth was measured and the extract then treated with cyanide to remove the copper complex; re-measurement of the remaining absorption, due to bismuth alone, permitted evaluation of the colour of the copper complex by difference.

Nielsch and Böltz[25] described a photometric determination of copper with EDTA, suitable for copper in tin- and nickel-containing alloys. Copper could be determined by its blue complex with EDTA in both faintly acid and alkaline solutions, using separate calibration curves in both cases. The extraction was independent of *p*H between 4·8 and 6·5 and almost independent of *p*H at 10, and was measured at 720 mμ. A wide choice of acids for dissolving the sample and of buffers for *p*H regulation was available, and by correct choice of conditions 0·035–8·0 mg./ml. of copper could be determined. No details of the application of the method to alloys are available.

Nielsch[26] determined copper in copper alloys using EDTA, but no details are available. Again, the same author[27] proposed a new photometric procedure for determining copper in aluminium alloys with EDTA, but details are lacking.

Amin[28] determined copper and silver in coinage. He found that copper could be titrated directly with EDTA in the presence of silver, because copper formed the more stable EDTA complex. The sample was dissolved in nitric acid, evaporated to dryness and the copper then titrated in ammoniacal solution with EDTA, using murexide as indicator. The determination was done on a micro scale, starting with 4–5 mg. of coinage.

In a further paper, Amin[4] determined copper in copper and aluminium alloys. (The determination of aluminium is described under the section on aluminium.) After separation of the copper by thioacetamide, the precipitate was dissolved in nitric acid and titrated in ammoniacal solution with EDTA, using murexide as indicator. If only the percentage of copper in the alloy was required, it could be titrated with EDTA directly, with murexide as indicator, because aluminium does not interfere in the titration.

Sir and Pribil[29] analysed iron-aluminium-copper alloys by two procedures. In the first method, the alloy was dissolved in bromine, hydrochloric acid, the solution taken to dryness after the addition of potassium chloride and the residue taken up in dilute hydrochloric acid. Copper was precipitated with hydrogen sulphide, filtered, ashed, dissolved in hydrochloric acid and freed from co-precipitated iron and aluminium by a precipitation with pyridine. The mixed hydroxides were filtered and the copper determined in the filtrate by direct titration with EDTA, using pyrocatechol violet as indicator, to the light blue or yellow-green end point.

In the second method, an aliquot of the solution of the metal was treated with excess EDTA, and the sum of copper, iron, and aluminium determined by back-titration with standard copper sulphate solution in pyridine medium, using pyrocatechol violet as indicator. In another aliquot, the sum of copper and iron was similarly determined after screening the aluminium with ammonium fluoride. A third portion was treated with excess EDTA and the copper precipitated as oxinate, which was filtered and ashed. The copper oxide so formed was dissolved in a little hydrochloric acid, diluted and titrated with EDTA to the pyrocatechol violet or murexide end point. From these three titrations, the values of the individual components, copper, iron and aluminium could be calculated.

Gallium

Milner[30] described the determination of gallium in alloys, after the preliminary separation of the element from chloride solution with diethyl ether. After washing the combined ether extracts with a sulphuric acid, ammonium chloride solution, the gallium was extracted into water and titrated at *p*H 2·8, using gallocyanine as indicator, to the change from blue to red. The procedure was for the direct determination of gallium over the range 0·25–50 mg. : iron interfered in the method.

In a further communication, Milner[31] described the direct determination of gallium in binary uranium-gallium alloys. The alloy was dissolved in nitric acid, evaporated to fumes with sulphuric acid, and diluted with water. A calculated excess of EDTA was added to complex the gallium and the excess back-titrated with standard iron solution at *p*H 2·2, using potassium benzohydroxamate as indicator. The end point was detected spectrophotometrically in an E.E.L. absorptiometer. Results were quoted over the range 8·6–78·4% of gallium for four alloy samples. In this method, the uranium was determined first, so that the gallium content was known by difference, to enable the calculated amount of EDTA to be added in its determination.

Gold

Kinnunen and Merikanto[32] described the complexometric determination of gold in gold alloys and in platinum metal. Gold was made to displace nickel from the potassium nickel tetracyanide complex, which was then determined by adding an excess of EDTA and back-titrating with standard manganous sulphate solution, using Eriochrome Black T as indicator. The alloy was dissolved in *aqua regia*, any silver filtered off, and the gold extracted in hydrochloric acid solution with diethyl ether. The combined extracts were then evaporated down with hydrochloric acid and nitric acid, the free acid neutralised, and solid potassium nickel tetracyanide added to liberate nickel ions, in the presence of an ammonia, ammonium chloride buffer. The advantage claimed was that gold could be accurately determined by the method without cupellation. Palladium could also be determined by a similar procedure.

Indium

Dolezal, Sir and Janacek[33] described the analysis of a silver-indium alloy (9 : 1) for indium. After dissolution of the alloy in nitric acid, the solution was treated with excess EDTA, pyridine and pyrocatechol violet indicator. The light yellow solution was then titrated with standard copper sulphate solution to a deep blue colour. The result agreed with that of a gravimetric determination via the oxinate.

The method was also considered suitable for the determination of indium in special lead alloys, after separation of lead as the sulphate and the masking of small amounts of cadmium—no details were given. Various other methods were described for the complexometric determination of indium in the above paper, without being specifically used for metallurgical purposes.

Iron

Schneider and Janko[34] determined iron in zirconium metal powder. The sample was dissolved in a platinium crucible in hydrofluoric acid, the melt taken up in water and EDTA added, followed by ammonia to make alkaline. The ammoniacal fluoride solution was separated from zirconium and thorium by hydrogen peroxide, filtered, and the iron determined colorimetrically at 525 mμ in the filtrate, by virtue of the violet complex formed with EDTA and hydrogen peroxide in ammoniacal solution.

Holmes[35] showed that traces of iron (5–50 p.p.m.) could be determined in bismuth metal by the well-known 1 : 10—phenanthroline procedure, if EDTA were present as a masking agent to obviate the effect of bismuth on colour development.

The paper by Sir and Pribil,[29] outlined under "Copper," described the determination of iron. The mixed hydroxides of iron and aluminium were dissolved in hydrochloric acid and added to the main filtrate. An aliquot of the filtrate was treated with excess EDTA, pyridine and pyrocatechol violet. The excess EDTA was titrated with standard copper solution, giving the total iron and aluminium content. Another portion of the filtrate was treated similarly, but with the addition of aluminium fluoride to mask the aluminium. The EDTA titration here gave the iron content directly, leaving the aluminium to be calculated by difference.

Lead

Kinnunen and Wennerstrand[36] determined copper, lead, zinc and iron in concentrates, brasses and gunmetals. After iodimetric titration of copper and iron, lead (and manganese) were titrated with EDTA in ammoniacal solution, after the addition of mannitol, ascorbic acid, potassium cyanide and 5–10 ml. of the manganese-EDTA complex. If aluminium were present, ammonium fluoride was added to the ammoniacal solution, the solution heated to boiling, cooled and then titrated as above. Alternatively, sulphosalicylic acid could be used instead of ammonium fluoride.

The same workers[37] reported upon the complexometric determination of lead in metallurgical products such as brass, zinc ore and lead concentrates. The procedures depended on the selective extraction of the lead diethyl-

dithiocarbamate complex and subsequent titration with EDTA.

In brasses and bronzes, the lead diethyldithiocarbamate was extracted by chloroform from ammoniacal solution in the presence of potassium cyanide and Rochelle salt. The combined extracts were titrated with EDTA in the presence of Rochelle salt and potassium cyanide, using Eriochrome Black T as indicator. Manganese interfered, but this could be minimised by excess potassium cyanide. Good figures were quoted for three brasses containing from 0·02–0·75% of lead.

A similar extraction procedure was described for lead concentrates; interference from bismuth was negligible if extraction took place from a sodium hydroxide, cyanide solution. Alternatively, the sample could be decomposed by sulphuric acid, the precipitated lead sulphate filtered off and titrated with EDTA.

A method was also described for the determination of lead in barium ores and figures quoted for zinc ores. It was claimed that all the above procedures were superior to those normally employing lead sulphate separation, in that the solubility errors inherent in lead sulphate precipitation were avoided.

Kinnunen and Merikanto[38] also reported briefly on the determination of lead in bronze and brass, although they stated that in these particular cases the lead estimation was usually omitted. The main constituents determined in this particular case were aluminium and zinc, the lead being determined after the aluminium titration by addition of either sodium diethyldithiocarbamate or 2 : 3-dimercapto-propanol-1 solution, when the liberated EDTA was titrated with a 0·005 M manganous sulphate solution, using Eriochrome Black T as indicator.

Pinkston and Kenner[39] described the determination of lead in lead-base alloys and lead drosses, using EDTA. The sample was dissolved in sulphuric acid, in the presence of filter paper to aid in the reduction and solution of antimony. Nitric acid was added to destroy the paper, the solution diluted, and tartaric acid added. After boiling, the precipitate of lead sulphate was filtered off, washed and then boiled with ammonium acetate solution to dissolve the precipitate. The lead was then titrated with EDTA in the presence of tartaric acid and ammonia, using Eriochrome Black T as indicator. The end-point change, which was somewhat obscure at room temperature, was much improved by titration at 70–80° C., being from pink to sky blue.

Barium and calcium interfered, but otherwise the method was claimed as rapid, simple, accurate and precise. Good results were quoted for N.B.S. solder (about 70% lead), N.B.S. lead-base bearing metal (about 84% lead), lead metal, and a variety of lead smelter samples—such as battery mud, drosses, etc.—containing upwards of 66% of lead.

Jenickova, Malat and Suk[40] discovered that pyrogallol- and bromopyrogallol red could be used as indicators in the complexometric determination of lead in sodium acetate solution. The method was applied to lead alloys. A lead-silver alloy containing 82·6% lead, 9·5% silver and small amounts of antimony, and one containing 48·8% lead, 4·5% cadmium and 33% iron, were analysed. If the sample contained large amounts of antimony, it was dissolved in hydrochloric acid and fumed with sulphuric acid. The separated lead sulphate was dissolved in ammoniacal ammonium acetate solution and an aliquot titrated with EDTA to the change from violet or blue-violet to light red, using either of the above chemicals as indicator. If the antimony content were low, the sample could be dissolved directly in sulphuric acid, then proceeding as above. The average error for the lead estimation in the above determination was ±0·28%.

Magnesium

Magnesium was determined in metallic titanium by Feszl.[41] The titanium was dissolved in dilute sulphuric acid, and the titanium separated off at *p*H 4–5 by hydrolysis. After filtration, magnesium was titrated in the filtrate by EDTA in the usual way, after prior separation of iron and manganese.

The Japanese workers Kodama and Kanie[42] described the complexometric determination of magnesium in aluminium alloys. The magnesium was separated from silicon (by sulphuric acid), from aluminium, chromium, copper and nickel (by sodium hydroxide and sodium chloride), and then from the remaining aluminium and iron by ammonia and ammonium chloride. The magnesium was then titrated with EDTA.

Beranek[43] determined magnesium in aluminium alloys with EDTA. For materials containing 0·4% or more of magnesium, no separation was necessary, aluminium, copper, zinc, iron, nickel and manganese being masked by triethanolamine and potassium cyanide in a solution cooled to 15°C. The titration was carried out with EDTA in a hydroxylamine hydrochloride reducing environment at *p*H 10.

Magnesium Oxide

Allsopp[44] determined magnesium oxide in magnesium metal. Magnesium metal was separated from any magnesium oxide present by sublimation in vacuum and the residue was dissolved in dilute hydrochloric acid. Aluminium and iron were removed as the hydroxides, and magnesium determined on an aliquot of the filtrate by titration with EDTA, using Eriochrome Black T as indicator. The method was applicable up to a magnesium oxide content of about 6%.

Manganese

Pribil and Vulterin[45] showed that in the presence of 1 : 2-diaminocyclohexane-N-N-N′-N′-tetra-acetic acid, tervalent manganese formed a stable, intense red complex in weakly acid solution. This complex could be determined iodometrically. Iron, copper and other cations were complexed and did not interfere. The method was successfully applied to the rapid determination of manganese in alloys and ores containing from 1 to 82% of manganese.

The sample was decomposed by acid or by alkaline fusion, an aliquot treated with the complexing agent, the *p*H adjusted to 5, glacial acetic acid and calcium acetate added, and the manganese oxidised to the tervalent state with lead dioxide. The mixture was filtered, potassium iodide added, and the liberated iodine titrated with sodium thiosulphate. The complex of tervalent manganese with 1 : 2-diaminocyclohexane-N-N-N′-N′-tetra-acetic acid exhibited maximum absorption at 500 mμ, and could be used for the colorimetric determination of manganese.

Kinnunen and Merikanto[46] applied the method of Flaschka for the determination of manganese to ferro-manganese, manganese copper, bronzes, brasses and steels. Manganese could be titrated with EDTA in hot ammoniacal solution buffered at *p*H 8–10 in the presence of a reducing agent such as ascorbic acid. Iron in moderate amounts, as well as heavy metals such as copper

zinc, nickel, cobalt, cadmium, mercury, etc., could be masked by potassium cyanide in a slightly acid, reduced system. A great excess of cyanide had to be avoided because of the danger of masking manganese.

If large quantities of iron were present, it was necessary to separate the iron. This could be accomplished either by extraction of the iron with amyl acetate or the manganese as the thiocyanate by a butyl phosphate-ether solvent. Aluminium could also be masked by various reagents. Lead was co-titrated with manganese by EDTA; it could be precipitated before titration with sodium diethyldithiocarbamate. For copper-base alloys, manganese was best titrated directly after the usual iodometric determination of copper.

Excellent results were quoted for various bronzes containing from about 0·15 to 1·3% of manganese.

Molybdenum

De Sousa[47] separated molybdenum by precipitation as calcium molybdate with calcium chloride. The precipitate was dissolved in hydrochloric acid, and on evaporating the solution a mixture of molybdic acid and calcium chloride was obtained. The calcium was then determined by complexometric titration with EDTA, using murexide as indicator, which thus gave an indirect determination of the molybdenum present. The method was considered suitable for molybdenum alloys and ores, but no results or details were quoted.

Nickel

Pribil[48] solved the problem of the determination of the nickel content of Raney nickel. The interference of aluminium was avoided by adding a large excess of ammonia, when the precipitated aluminium hydroxide redissolved. In these circumstances, nickel could be accurately determined by titration with EDTA, using murexide as indicator. Alternatively, aluminium could be screened with triethanolamine. No details were described.

The German workers Nielsch and Böltz[49] showed that high concentrations of nickel could be determined photometrically with EDTA, working at a *p*H between 4·6 and 6·8 and using a filter photometer. The solution was buffered to *p*H 5·3 with sodium acetate; high concentrations of ammonium salts hindered the measurement. The Lambert-Beer Law was followed for nickel concentrations between 40 and 5,000 mg/100 ml. The method was considered suitable for alloys rich in nickel, especially Monel metal, but no details were given.

Selenium

The method of Cheng[81] for the determination of traces of selenium in stainless steel, (described in the ferrous section of this review) was successfully applied to high purity copper.

Silver

As described above, Amin[26] determined copper in silver coinage. In the same alloy, silver was determined after the copper titration by the addition of potassium nickel tetracyanide, when the reaction of the silver ions with the complex cyanide yielded a corresponding amount of nickel, which changed the murexide indicator from red to yellow. The liberated nickel was then titrated with EDTA to a permanent purple-red colour, the volume of EDTA used being equivalent to the silver in the sample.

Nordling[50] used EDTA as a masking agent in the gravimetric determination of silver in refined bismuth, using the 1 : 2 : 3-benzotriazole procedure. He showed that bismuth did not interfere and that in ammoniacal solution it was possible to determine from 0·01 to 0·10% silver in refined bismuth by the method.

Malinek[51] determined silver in refinery slags by gravimetric determination with mercapto (phenylthio) thiadiazolone, the method being made more selective by precipitation in the presence of EDTA in ammoniacal solution.

Thorium

Furby[52] determined the thorium content of thorium-uranium alloys containing less than 60% of uranium by direct titration with EDTA, using alizarin red S as indicator. This procedure was based on the original work of Fritz and Ford, who titrated thorium at *p*H 2·8 with EDTA until the red colour of the alizarin R-thorium lake was discharged. For alloys containing more than 60% of uranium, preliminary separation of thorium proved necessary. This involved the precipitation of thorium as thorium benzoate in the range 1·5–2·5, dissolution of the precipitate in hydrochloric acid after filtration and addition of excess EDTA. The excess EDTA was then back-titrated with standard ferric iron solution, with salicylic acid as indicator.

Milner and Sneddon[53] similarly analysed thorium-cerium alloys for thorium, without chemical separation, in a perchloric acid solution at *p*H 2·2; the alloy could contain from 1–99% of either metal. At this *p*H, cerous ions were not complexed by EDTA, and an excess of EDTA was added to complex the thorium, followed by back-titration with standard thorium perchlorate solution, using Eriochrome Cyanine as indicator and plotting the end-point photometrically. The error claimed was less than ± 1%; iron interfered in the determination.

Milner and Barnett[54] determined thorium in binary thorium-tungsten alloys by adding excess EDTA and back-titrating with standard thorium solution, using alizarin red S as indicator. The interference of tungsten was prevented by the addition of hydrogen peroxide.

Milner and Woodhead[55] used a solvent extraction of thorium nitrate into mesityl oxide to separate thorium from other alloy constituents. The sample solution was saturated with calcium nitrate to facilitate the separation and the method was applied to the determination of thorium in thorium-aluminium alloys. In the cases where solvent extraction was inapplicable, for instance in the case of alloys containing zirconium, it was possible to separate thorium by precipitation as the fluoride from 10 M hydrofluoric acid solution. Milner and Barnett[56] utilised the method in the analysis of thorium-zirconium and uranium-thorium-zirconium alloys. The fluoride precipitate was centrifuged off, washed, and dissolved in perchloric acid. The precipitate was then treated with a slight excess of EDTA in an acetate-buffered solution at *p*H 5 containing boric acid to complex any traces of fluoride ions present. The excess EDTA was then titrated with standard iron solution, with salicylic acid as indicator.

Banks and Edwards[57] proposed to determine thorium in thorium-aluminium alloys by extraction of thorium from nitric acid solution into mesityl oxide. This extraction was quantitative if the solvent were nearly saturated with lithium nitrate. The extracted thorium was then titrated with EDTA, using a spectrophotometric end-point in the following manner. Initial spectrophotometric titrations of EDTA with standard thorium

nitrate (Chrome Azurol S as indicator) served to establish a calibration curve. The unknown amount of thorium was then added to the same quantities of EDTA and indicator as were present in the initial titration, and the titration continued to a point beyond the end-point with the same standard thorium solution. The total thorium corresponding to the optical density of this solution could then readily be obtained from the calibration curve. From the total thorium present and the volume of standard thorium solution added, the unknown amount of thorium was calculated. The method had the advantage of requiring only one standard solution, one *p*H adjustment, and the measurement of a single optical density for each thorium determination. The method was considered ideal for the analysis of many thorium-aluminium alloys on a routine basis, but no actual alloy analysis figures were quoted by Banks and Edwards.

Schneider[58] determined thorium and thorium oxide in the cathodes of thoriated tungsten used for radio valves of high efficiency. The material was treated with hydrofluoric and nitric acids; the thorium dioxide remained undissolved and part of the thorium fluoride was also precipitated. The latter dissolved when the solution was treated with EDTA and ammonium hydroxide at 90° C. The undissolved thoria was filtered off and the filtrate treated with hydrogen peroxide. The peroxyhydrate precipitate was then converted to the oxide or dissolved in hydrochloric acid and titrated with EDTA, using pyrocatechol violet as indicator.

Tin

Kinnunen and Wennerstrand[59] determined tin in copper-base alloys by complexometric methods. For tin bronzes and gun metals the sample was dissolved in concentrated hydrochloric acid, and an excess of EDTA solution added together with a saturated solution of thiourea to prevent interference from copper. The *p*H was adjusted to 2, xylenol orange indicator added, and the excess of EDTA back-titrated with thorium nitrate solution to the change from yellow to red.

For tin alloys, the sample was dissolved in hydrochloric acid and hydrogen peroxide, and an aliquot treated with an excess of EDTA solution. The solution was heated to boiling, adjusted to *p*H 5, and potassium ferro-ferricyanide solution and 3 : 3′-dimethylnaphthidine indicator added. The excess of EDTA was titrated with zinc acetate solution. Solid ammonium fluoride was then added to displace tin from the tin-EDTA complex and the displaced EDTA titrated further with zinc acetate solution, thus giving a measure of the tin present in the original alloy. The method was rapid and excellent results were quoted for tin bronzes containing from 0·5–11% of tin, for a tin alloy containing about 41% of tin, and for a gun metal containing 5% of tin.

Titanium

EDTA was used as a screening agent in the photometric determination of titanium in uranium by Henicksman.[60] The titanium was held in solution with EDTA and the uranium was precipitated at *p*H 2 with hydrogen peroxide. The titanium was then determined by the usual hydrogen peroxide method, over a range of 0·3–1·0% titanium. Vanadium interfered in this determination.

Uranium

Milner and Edwards[61] described the application of EDTA in the determination of uranium in metallurgical alloys, which contained this element as a minor constituent. The uranium was initially separated from the sample solution by precipitation as uranyl ammonium phosphate in the presence of EDTA. By this method, uranium could be separated from many elements complexed by EDTA under these conditions, including iron, chromium, copper, nickel, vanadium, cerium and bismuth. The precipitate was separated by centrifuging, dissolved in hydrochloric acid and the resulting solution passed through a lead reductor. The tetravalent uranium was then titrated with standard ceric sulphate solution, using ferroin as indicator. The method proved suitable for bismuth-uranium alloys containing from 3·5 up to 20% of uranium, and could be adapted for samples containing down to 0·5% of uranium.

Shelton[16] also published a method for the determination of uranium in uranium-bismuth alloys (see under bismuth). The uranium was separated by precipitation as the oxine complex after the addition of EDTA to form soluble metal-EDTA complexes. Under these conditions, bismuth did not interfere. The uranium was then determined by a direct gravimetric determination on the filtered precipitate. The procedure could be adapted for alloys containing a lower limit of 0·5% of uranium.

Zinc

Sergeant[62] described in this journal the complexometric determination of zinc in aluminium alloys. The alloy was dissolved in nitric, hydrochloric acid mixture, with tartaric acid to prevent precipitation of aluminium, iron, etc. Nitric acid was added and sodium sulphide, sodium carbonate mixture to precipate zinc sulphide, together with nickel and copper, over a *p*H range of 4·5–7·0. The whole was filtered and dissolved in hydrochloric acid. Sulphur was then removed by bromine oxidation and iron and aluminium by making the solution ammoniacal. These were filtered and the filtrate treated with potassium cyanide to complex copper and nickel. On adding formaldehyde, the zinc complex was decomposed and was titrated with EDTA, using Eriochrome Black T as indicator. Results for alloys containing from 0·12 to 9·25% zinc were recorded. The advantage claimed for the method was the rapid quantitative precipitation of zinc sulphide by the sodium carbonate, sodium sulphide reagent at *p*H 4·5–7·0 in an easily filterable form.

As an alternative method for this determination, Rees and Hartley[63] described an ion-exchange separation for the removal of other alloy constituents from the zinc before the titration with EDTA was carried out.

In his review paper, Pribil[64] mentioned the complexometric determination of zinc in aluminium alloys. This was accomplished by extracting zinc diethyldithiocarbamate into ethyl acetate, and displacing the zinc from the organic phase by a weak solution of mercuric chloride. The zinc was now present in aqueous solution together with a definite amount of mercuric chloride. Both cations were complexed with potassium cyanide and then the zinc selectively demasked with chloral hydrate and titrated with EDTA. No details of the procedure were given.

Fritz and co-workers'[5] described the analysis of uranium-zinc alloys containing up to 20% uranium. An aliquot of the solution in hydrochloric acid and hydrogen peroxide was adjusted to *p*H 8–8·5 with either hydrochloric acid or sodium hydroxide, after the addition of sodium bicarbonate to hold the uranium in solution as a complex. An excess of standard EDTA was added and the excess

back-titrated with zinc chloride solution, using ammonium purpurate (murexide) as indicator, to the change from magenta to orange. Ammonium purpurate was preferred to Eriochrome Black T as indicator in this determination, because of the interference of uranium with the Eriochrome end-point.

In the determination of zinc in aluminium bronzes, Amin[66] used thioacetamide to separate zinc as zinc sulphide from strongly alkaline solutions. This procedure had the advantage of separating off the sulphide in a coarse, easily filterable form. After washing the precipitate with an alkaline thioacetamide solution, it was dissolved in dilute hydrochloric acid and an aliquot buffered to *p*H 10 with ammonia, ammonium chloride solution. Potassium cyanide was added to mask traces of any other metal present, and the zinc selectively demasked with formaldehyde and titrated directly with EDTA to the Eriochrome Black T end-point. Various precautions to be taken in the method were enumerated. Six samples of aluminium bronze could be analysed for zinc in three hours by the method, and satisfactory results were quoted for three samples ranging from 4·13 to 7·36% of zinc.

Kinnunen and Merikanto[5] described the determination of zinc in bronzes and brasses, in conjunction with the determination of aluminium and lead described above. After titration of the aluminium and lead, the zinc was demasked from the cyanide complex with formaldehyde and titrated with EDTA, using Eriochrome Black T as indicator. Cadmium interfered in this determination, being titrated with the zinc.

Chew and Lindley[67] described in METALLURGIA the chromatographic separation of zinc from copper-base alloys containing 1–40% zinc, and its subsequent volumetric determination with EDTA. The sample was dissolved in *aqua regia*, evaporated almost to dryness, and redissolved in a solvent consisting of 96 parts of butanol and 4 parts of 20% v/v hydrochloric acid. The solution was run through a moderately tightly packed 7 in. column of cellulose and then the eluate concentrated by evaporation and cooled. The solution was then titrated at *p*H 10 with EDTA, Eriochrome Black T as indicator.

After the determination of lead in the paper described earlier, Kinnunen and Wennerstrand[37] determined zinc by adding formaldehyde and titrating with EDTA in the usual manner, adding more formalin if necessary. The methods described permitted the determination of copper, lead and zinc in leaded brass from the same initial weight. If the lead and zinc contents were low, the method failed, and it was then necessary to extract the lead and zinc with diethyldithiocarbamate.

Zirconium

Notable advances have been made recently in the analytical chemistry of zirconium, in that several volumetric determinations using EDTA have been reported, including applications to metallurgical analysis.

Milner and Phennah[68] discovered that zirconium could be determined in acid solution (*p*H 5–6) by the addition of excess EDTA solution and boiling to complete the reaction. After cooling, the solution was back-titrated with standard iron solution, using salicylic acid as indicator. It was possible to determine up to at least 100 mg. of zirconium with an accuracy of about ± 1%. The main error involved was the personal one of deciding the end-point change from yellow to brown.

The method was applied to uranium-zirconium alloys by dissolving the alloy in nitric acid and hydrofluoric acid and then fuming down with perchloric acid. The zirconium was then precipitated as the insoluble zirconium mandelate, filtered, dissolved in dilute sulphuric acid and the zirconium titration completed as described above. Results were quoted for alloys containing from 2·2 to 59% of zirconium.

Milner and Edwards[69] described a more accurate method for the determination of zirconium in various alloy systems. An excess of EDTA was added to complex the zirconium and the unused EDTA titrated with standard ferric iron solution, the end-point being determined photometrically using an E.E.L. absorptiometer. Sodium salicylate was used as indicator in the *p*H range 3–7 and potassium benzohydroxamate for the *p*H range 1·8–3·3. Under these conditions, it was possible to determine zirconium in amounts up to 100 mg. with an accuracy of ± 0·6% or better. Uranyl ions did not interfere with the titration at *p*H 2, and the method could be adapted to the determination of zirconium in uranium-zirconium alloys containing from 2 to 60% of zirconium. There was good agreement between the EDTA method and a gravimetric method published previously, but the volumetric method was recommended on the score of speed and accuracy.

Milner and Sneddon[70] published a similar method for determining the cerium content of cerium-zirconium alloys; this depended on the fact that cerous ions did not form a complex with EDTA at *p*H 2.

In many cases zirconium had to be separated from other alloying constituents before application of the EDTA titration. For instance, in the determination of zirconium in its binary alloys with niobium and tantalum, the method of Milner and Phennah[68] was inapplicable because at the *p*H of the titration hydrolysis of the earth acid elements occured and the resulting precipitate masked the end-point. Thus Milner and Edwards[71] initially removed the bulk of the niobium or tantalum by extraction with methyl isobutyl ketone (hexone) from a solution 10 M in hydrofluoric acid and 6 M in sulphuric acid. The zirconium was then separated from any unextracted earth acids by hydrogen peroxide. Under these conditions, both niobium and tantalum formed soluble peroxy complexes, whereas the zirconium was completely precipitated from solution. After separation of the precipitate by filtration, it was dissolved in hydrochloric acid and an excess of EDTA added. The *p*H was then adjusted to 5–6, the solution boiled, cooled, and the excess of EDTA titrated with ferric iron solution, using salicylic acid as indicator. The method was applied to synthetic niobium and tantalum alloys containing zirconium with ratios of Nb : Zr and Ta : Zr ranging from 100 : 1 to 1 : 1. The procedure was satisfactory in all cases. Care had to be taken to prevent tantalum coming out of solution during evaporation.

In a more general procedure, Milner and Barnett[72] showed that the separation of zirconium from the constituents of several alloys could be accomplished in many cases by precipitation as barium fluozirconate. This had the advantage that as hydrofluoric acid was often essential for complete dissolution of zirconium alloys, separation of zirconium could be accomplished without removal of fluoride ions from the solution.

After separation of the insoluble barium fluozirconate, the precipitate was dissolved in a mixture of nitric and boric acids and the zirconium precipitated therefrom as the hydroxide. This precipitate was separated, dissolved

in hydrofluoric acid, and the solution evaporated to fumes of perchloric acid to remove fluoride ions completely. An excess of standard EDTA was added and the zirconium determined as above at *p*H 2·3, using potassium benzohydroxamate as indicator and a photometric technique for end-point detection. The method was applicable to the determination of milligram amounts of fluoride-containing nitric or hydrochloric acid solutions, provided that the concentration of these acids was below 3N. It was suitable for the determination of zirconium in the presence of uranium, titanium, niobium, tantalum, molybdenum, tungsten, lead, iron, copper and tin.

The procedure was adapted for the following types of synthetic alloys: uranium-molybdenum-zirconium (U> 75%, Mo 5–15%, Zr 1–10%), uranium-titanium-zirconium (U>85%, Ti 1–15%, Zr 1–15%) and uranium-niobium-zirconium (U 50–80%, Nb 1–40%, Zr 1–40%). Good recoveries of zirconium were reported in all cases.

FERROUS APPLICATIONS

Aluminium

Elliott and Robinson[73] described the determination of aluminium in plain steel. The bulk of the iron was separated by extraction from hydrochloric acid solution with dichlorodiethyl ether. The aluminium was separated from metals such as copper, nickel, manganese and cobalt by the addition of ammonia, ammonium chloride solution. After filtration, the precipitate was redissolved in acid, and EDTA was added: this complexed the metals present. The solution was then made alkaline with potassium hydroxide to *p*H 11, a few drops of hydrogen peroxide added and the precipitate containing the last traces of iron and manganese filtered off. The aluminium was then determined gravimetrically in the filtrate via 8-hydroxyquinoline.

Johannsen, Bobowski and Wehber[74] determined aluminium in ferrotitanium by a complexometric procedure. The ferrotitanium was dissolved in hydrochloric acid, oxidised with nitric acid and the solution, after dilution, treated with an excess of solid sodium hydroxide. The whole was filtered and an aliquot of the filtrate treated with hydrochloric acid to give *p*H 1. A little oxalic acid was added, to avoid interference by manganese, and then 20 ml. of standard EDTA solution, keeping the solution at about 40° C. The solution was then buffered to about *p*H 5·5 with sodium acetate, and solid ammonium thiocyanate added, followed by the indicator Variamine blue B-base (4-amino-4′-methoxydiphenylamine). The excess EDTA was then back-titrated with a volumetric solution containing zinc chloride and cupric chloride, to the indicator change to violet.

For details of the theoretical background of the EDTA titration of the aluminium determination proposed by Johannsen *et al*, the original paper should be consulted. Figures were quoted for ferrotitanium samples containing about 4, 6·5 and 9% of aluminium, respectively. The method compared very well in time and accuracy with procedures utilising precipitation with ammonia or 8-hydroxyquinoline and ignition to aluminium oxide, or bromometric titration of the dissolved oxide precipitate.

Claasen, Bastings and Visser[3] described the use of EDTA as a masking agent in the spectrophotometric determination of aluminium with 8-hydroxyquinoline and its application to iron and steel analysis. These authors found that aluminium hydroxyquinolate could be quantitatively extracted by chloroform from an ammoniacal solution containing 8-hydroxyquinoline, potassium cyanide and EDTA. Alternative procedures were described to obviate the interference of titanium, vanadium, tantalum, niobium, uranium, zirconium, gallium, bismuth, antimony and beryllium, and in these circumstances the method was practically specific for aluminium. Excellent results were quoted for the determination of both total and acid-soluble aluminium in a large variety of alloy steels containing from about 0·003 to 7% of aluminium.

Beryllium

Belohlavek[75] used the free acid of EDTA as a screening agent in the determination of beryllium in steel. The steel was dissolved in hydrochloric acid, evaporated, separated from silica, and the filtrate evaporated to dryness. The residue was ignited, fused with sodium peroxide, dissolved in water and filtered. After the addition of the EDTA complexing agent, the beryllium was precipitated with sodium hydroxide, interfering elements remaining in solution.

Cobalt

The Belgian workers Wyndaele and Verbeek[76] used EDTA as a masking agent in the polarographic determination of cobalt in steel. The method was based on the reduction of cobalt^{III} to cobalt^{II} after the oxidation of cobalt^{II} by lead dioxide. Interfering elements were precipitated with pyridine.

Copper

The determination of copper in various non-ferrous alloys described by Cluley[24] was applied to several steels. These were a 0·03% carbon steel (B.C.S. No. 150), a high-speed steel (B.C.S. No. 241), and an 18–8 stainless steel (B.C.S. No. 235). Small amounts of copper, from 0·065–0·98%, were successfully determined in these materials, and the modified procedure was also suitable in the presence of up to 20% of bismuth added to these samples. In addition, good results were obtained with three iron-nickel-copper alloys, containing 0·5, 1·0 and 1·5% of copper, respectively.

Magnesium

Green[77] determined magnesium in nodular cast iron with EDTA. Magnesium was separated from interfering elements by zinc oxide but no further details are given in the available abstract.

Reichert[78] determined magnesium in iron by a complexometric titration procedure. The iron was dissolved in a mixture of hydrochloric and nitric acids, the solution made ammoniacal, and ammonium chloride added. Hydrogen sulphide was passed in and the precipitate filtered and washed. Ascorbic acid, potassium cyanide solution and triethanolamine were added to the hot filtrate. After the addition of further ascorbic acid, the magnesium was titrated at 60° C. and *p*H 10 with EDTA, using Eriochrome Black T as indicator.

Manganese

In the non-ferrous section of this review, the procedure of Kinnunen and Wennerstrand[46] for the determination of manganese in manganese copper, bronzes and brasses was discussed. This work was also applied to the determination of manganese in ferromanganese and steels. The steel was dissolved in *aqua regia*, fumed down with sulphuric acid and the residue dissolved in

hydrochloric acid. The bulk of the iron was then separated off by solution into amyl acetate, and the extract titrated for manganese with EDTA after adding ascorbic acid, potassium cyanide and ammonia to make the solution alkaline.

Alternatively, the manganese was separated from the iron solution as the thiocyanate into a butyl phosphate, ether mixture, using ammonium hydrogen fluoride to mask aluminium and traces of iron. The combined extracts were then acidified with hydrochloric acid, when manganese passed into the acid layer. The acid layer was then practically neutralised with ammonia and the manganese titrated as above.

Results were quoted for ferromanganese containing about 74% of manganese and for a steel with about 1% of manganese.

Flaschka, Amin and Zaki[79] showed that it was possible to separate manganese from iron and aluminium using a zinc oxide procedure. Manganese in the filtrate was then titrated with EDTA on a micro scale, after masking any zinc, nickel, cobalt, copper or cadmium by potassium cyanide. It was stated that manganese could be quantitatively determined by this procedure in steels and other ferrous alloys, but no details were given.

The complexometric determination of manganese in spiegeleisen and other ferromanganese alloys was described in two procedures by Flaschka and Püschel.[80] In the first procedure the diluted solution of the alloy in *aqua regia* was filtered and an aliquot treated with ascorbic acid until the yellow colour of the ferric ion disappeared. Diluted ammonia was added to a faint persistent turbidity, followed by potassium cyanide and a measured excess of EDTA. The solution was brought to the boil, diluted, ammonia, ammonium chloride buffer added, followed by Tiron solution (i.e., 1 : 2-dihydroxy-3 : 5-benzenedisulphonic acid) to mask titanium and aluminium, and Eriochrome Black T indicator. The excess EDTA was then back-titrated with standard magnesium solution to the end-point blue-green to red.

This procedure was considered suitable for the determination of small as well as moderately large amounts of manganese in the presence of not too large an amount of iron. Spiegeleisen could not be analysed by this procedure because the ratio of iron to manganese was large. Procedure 2 was used in these circumstances, involving a preliminary separation of manganese by the chlorate procedure. The separation was not perfect and merely served to reduce the ratio of iron to manganese to a value which permitted the use of Procedure 1.

Procedure 2 involved dissolution of the sample in nitric acid and evaporation of an aliquot of the solution to a small volume. Small amounts of potassium chlorate were then added to precipitate manganese dioxide, which was filtered off on a porous porcelain crucible. The precipitate was dissolved in hydrochloric acid, completing the dissolution with the aid of hydroxylamine hydrochloride. The solution was then treated as in Procedure 1, starting at the point of addition of ascorbic acid.

Selenium

Cheng[81] used EDTA as a masking agent in the determination of selenium in stainless steels and in high purity copper by means of 3 : 3′- diaminobenzidine. Large amounts of polyvalent metals such as iron and copper could be effectively masked by EDTA in the *p*H range 2–3 without affecting the piazselenol coloration. Low results were obtained in the presence of EDTA if the *p*H were allowed to rise over 3. The solubility of EDTA was limited in acidic medium, but the EDTA complexes of iron and copper were quite soluble in the *p*H range 2–3. After standing for 30 minutes, the *p*H was adjusted to 6–7, the complex extracted by toluene from the aqueous solution and the optical density measured at 420 mμ. Excellent results were quoted for the determination of selenium in the parts per million range, in both stainless steels and highly-refined copper.

Sulphur

Belcher, Gibbons and West[82] described the determination of sulphur in plain carbon steel. The steel was dissolved in a mixture of concentrated hydrochloric acid and nitric acid, evaporated to dryness, baked and taken up in concentrated hydrochloric acid. Ferric iron was then extracted by shaking with isoamyl acetate and the acid layer evaporated to dryness again to ensure that all silica was insolubilised. The sulphur was then precipitated as barium sulphate from the solution in hydrochloric acid, allowed to stand for 2 hours and filtered off on a paper-pulp pad. The washed barium sulphate was then dissolved in an excess of standard ammoniacal EDTA by boiling, and the excess EDTA back-titrated with standard magnesium chloride solution, using Eriochrome Black T as indicator.

Excellent results were quoted for steels containing 0·006–0·075% of sulphur. The main advantages claimed for this procedure over the British Standard method were increased speed and the absence of co-precipitated iron in the barium sulphate precipitate.

Miscellaneous

Jimeno and Redondo[83] used EDTA as a screening agent in the qualitative examination of special steels for the presence of tin, tungsten, chromium, vanadium, copper, titanium, molybdenum, nickel, cobalt and manganese.

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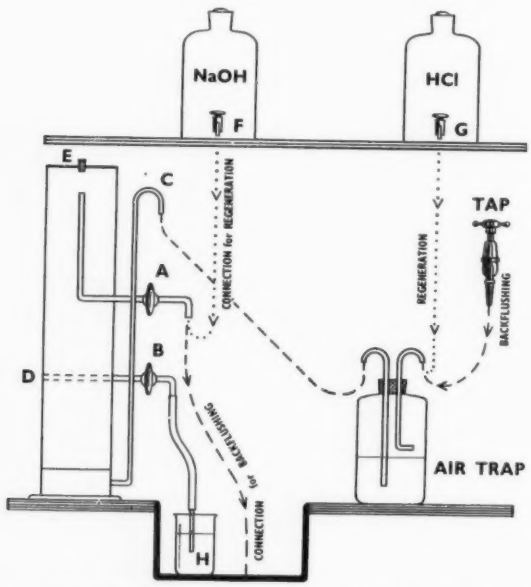
A Source of Very Pure Water

Laboratory Scale Deionising Column

WATER having a specific resistance within the range 3–15 × 10^6 ohms is finding an increasing application, not only in the laboratory, but also in industry, where such water is used in the preparation of pure chemicals and in the washing of components subsequent to treatment with acids and other electrolytes.

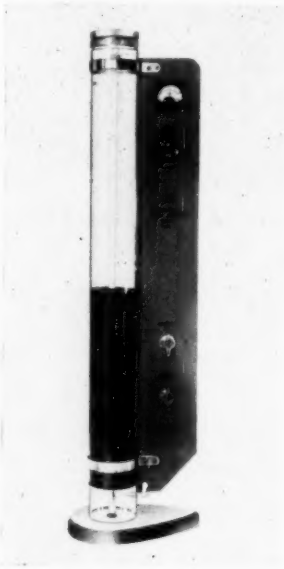
Water produced by simple distillation almost invariably contains significant traces of metal ions, dissolved carbon dioxide, and silica, and has a pH value which is always less than 7 and often as low as 5·9. Three or more distillations in glass are needed to produce what is known as "conductivity water", and even then such water has an acid reaction due to the difficulty of eliminating final traces of carbon dioxide and ions derived from the material of the still.

The advent of mixed resin ion exchange techniques made it possible to obtain, straight from the tap and at a fraction of the cost of commercially distilled water, effluent having a quality equivalent to that formerly realised only by triple vacuum distillation in quartz. Because of these advantages, mixed bed water deionisers have come to be used in all branches of industry where large quantities of pure water are required, and in which the ion exchange column can be made at least 12 in. in diameter. In smaller columns, difficulties were experienced in reclassifying and remixing the resins, and it was at first believed that the construction of columns suitable for laboratory use and designed for regeneration *in situ* would not be possible. As a result of these difficulties, mixed bed laboratory deionisers have been based on exchangeable cartridges which could be replaced on exhaustion, and while this method gives satisfying results, it is one which is inevitably expensive.



A	WATER STOPCOCK	E	RUBBER STOPPER
B	CENTRAL DISTRIBUTOR STOPCOCK	F	ALKALI STOPCOCK
C	DEIONISED WATER OUTLET	G	ACID STOPCOCK
D	CENTRAL DISTRIBUTOR	H	BEAKER

Diagrammatic arrangement showing regeneration process for Griffin-Raleigh water deioniser.



Griffin-Raleigh mixed resin ion-exchange unit

The Griffin-Raleigh deioniser marketed by Griffin & George, Ltd., has been developed as the result of an invention in ion exchange technique employing three resins instead of two, by means of which it is possible to regenerate *in situ* columns down to 3 in. in diameter. Using this equipment, the cost of purification is considerably less than that with cartridge type deionisers. The initial cost also compares favourably with the cartridge type units.

A built-in amplifier and bridge circuit incorporating a conductivity cell enables effluent quality to be monitored, and the circuit is independent of mains voltage and temperative fluctuations. Using mains water, flow rates of 5–20 gallon per hour may be used with an effluent conductivity of 0·2 micromho, with an output between regenerations of 16 and 64 gallons for the two sizes, respectively. Using as influent either single distilled or two-bed deionised water, the effluent conductivity may approach 0·05 micromho, and an inter-regeneration capacity of several thousand gallons is realised.